# KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
**COIMBATORE-21**
(For the candidates admitted from 2018 onwards)

# DEPARTMENT OF PHYSICS

---

**SUBJECT: THERMODYNAMICS AND STATISTICAL MECHANICS**
**SEMESTER: II**
**SUB.CODE:19PHP201** **CLASS: I M.Sc PHYSICS**

**Instruction Hours / week: L: 4 T: 0 P: 0** **Marks:** Internal: **40** External: **60** Total: **100**
**End Semester Exam:** 3 Hours

**Course Objectives**

- Thermodynamics is an important branch of physics, which helps us to understand the different phenomena in the evolution of the universe.
- This paper gives a basic idea about the laws of thermodynamics and statistical processes.

**Course Outcomes (COs)**

1. Identify and describe the statistical nature of concepts and laws in thermodynamics, in particular: entropy, temperature, chemical potential, Free energies, partition functions.
2. Use the statistical physics methods, such as Boltzmann distribution, Fermi-Dirac and Bose-Einstein distributions to solve problems in physical systems.
3. Apply the concepts and laws of thermodynamics to solve problems in thermodynamic systems such as gases, heat engines and refrigerators etc.

## UNITI- LAWS OF THERMODYNAMICS

Some consequences of the laws of thermodynamics − Entropy − Calculation of entropy changes in reversible processes. The principle of increase of entropy − Thermodynamic potentials − Ehthalpy, Helmholtz and the Gibbs functions − Phase transitions − The Clausius-Clayperon equation − Van der Waals equation of state.

## UNIT II- KINETIC THEORY

Distribution function and its evolution − Boltzmann transport equation and its validity − Boltzmann's H-theorem − Maxwell-Boltzmann distribution − Transport phenomena − Mean free path- Conservation laws − Hydrodynamics (No derivation).

## UNIT III- CLASSICAL STATISTICAL MECHANICS

Maxwell Boltzmann distribution law: Evaluation of constants - Maxwell's law of distribution of velocities - Most probable speed, Average speed, Root mean square speed - Principle of equipartition of energy - Partition function - Condition for applicability of M.B statistics - Non degenerate and degenerate systems - Maxwell velocity distribution in a given direction - Total internal energy of an ideal gas - Molar heat capacity of a gas at constant volume – Entropy - Helmholtz free energy - Pressure and equation of state of an ideal gas - Limitation of M.B method.

## UNIT IV- QUANTUM STATISTICAL MECHANICS

B.E energy distribution for energies in the range E to E + dE – Condition for B.E distribution to approach classical M.B distribution - Bose temperature - Bose Einstein condensation - Planck's law from B.E law - Fermi Dirac distribution law (no derivation) - FD law for the energies in the range E to E+dE – Fermi energy - Effect of temperature - Energy distribution curve - Free electron in a metal - Fermi temperature and Thermionic emission - Richardson Dushmann Equation - Comparison of MB,BE and FD statistics.

## UNIT V- APPLICATIONS OF QUANTUM STATISTICAL MECHANICS

Ideal Bose gas : Photons − Black body and Planck radiation − Photons − Specific heat of solids − Liquid Helium.
Ideal Fermi gas : Properties − Degeneracy − Electron gas − Pauli paramagnetism
Ferromagnetism : Ising and Heisenberg models.

## SUGGESTED READINGS:

1. Agarwal B.K. and M. Eisner, 3rd edition, 2013, Statistical Mechanics, New age international Limited, New Delhi.
2. Reif F., 2008, Fundamentals of Statistical and Thermal Physics, (Reprint), McGraw Hill International Edition, Singapore.
3. Gupta and Kumar, reprint, 2014, Elements of Statistical Mechanics, Pragati Prakashan, Meerut.
4. Huang K., 2nd edition, 2014, Statistical Mechanics, Wiley Eastern Limited, New Delhi
5. Sears N. and L. Salinger, 2013, Thermodynamics, 3rd Ed., Narosa Publishing House, New Delhi.
6. Greiner W., L. Neise and H. Stocker, 1st edition, 2007, Thermodynamics and Statistical Mechanics, Springer Verlag, New York.
7. Singh. K. and S.P. Singh reprint 2016, Elements of Statistical Mechanics, S. Chand & Company Ltd., New Delhi.

# UNIT-I

**Laws of Thermodynamics**: Some consequences of the laws of thermodynamics − Entropy − Calculation of entropy changes in reversible processes. The principle of increase of entropy − Thermodynamic potentials − Ehthalpy, Helmholtz and the Gibbs functions − Phase transitions − The Clausius-Clayperon equation − Van der Waals equation of state.

## THERMODYNAMICS

Thermodynamics is the science of studying the changes that occur within a system in relation to its interaction with its surroundings according to a series of laws formulated that are considered valid for all systems. Thermodynamics allows scientists to study the potential reactions and interactions of systems that exist only in theory, or be such that they cannot be recreated or contained in a laboratory for study.

The empirical facts of thermodynamics are comprehended in its four laws. The first law specifies that energy can be exchanged between physical systems as heat and thermodynamic work. The second law concerns a quantity called entropy, expresses limitations, arising from what is known as irreversibility, on the amount of thermodynamic work that can be delivered to an external system by a thermodynamic process.

## THERMODYNAMIC SYSTEMS

An important concept in thermodynamics is the “system”. A physical system is the region of the universe under study. A system is separated from the remainder of the universe by a boundary which may be imaginary or not, but which by convention delimits a finite region. The possible exchanges of work, heat, or matter between the system and the surroundings take place across this boundary. There are five dominant classes of systems:

1. Isolated Systems – matter and energy may not cross the boundary.
2. Adiabatic Systems – heat may not cross the boundary.
3. Diathermic Systems - heat may cross boundary.
4. Closed Systems – matter may not cross the boundary.

Open Systems – heat, work, and matter may cross the boundary.

## LAWS OF THERMODYNAMICS

The four main laws of Thermodynamics are,

***Zeroth Law*** - if two systems each are in equilibrium with a third system, then they must are also be in thermal equilibrium with each other.

***First Law*** - if heat is added to a system, some of that energy stays in the system and some leaves the system.

***Second Law*** - no reaction is 100% efficient and all energy wants to flow and spread to areas with less energy.

***Third Law*** - it is impossible to cool an object to absolute zero because all processes will cease before absolute zero is reached, this is commonly called the state of entropy.

## ENTROPY:

Entropy is a defined function of the thermal state of a body and is not affected in any way by the manner in which a particular state is reached. The change in entropy passing from one state A to another state B is given by $S_B - S_A = \int_A^B \frac{dQ}{T}$

where dQ is the quantity of heat absorbed or rejected at a temperature T in going from state A to state B.

(i) Entropy of a system remains constant during an adiabatic change,
(ii) Entropy of a system remains constant in all reversible processes.
(iii) Entropy of a system increases in all irreversible processes.

## CALCULATION OF ENTROPY:

*(i) Entropy of an ideal gas*

Consider n gram molecules of an ideal gas occupying a volume V at a pressure P and temperature T. Let quantity of heat dQ be given to the gas, then I law of thermodynamics is dQ=dU+dW. If $C_v$ is the heat capacity of gas at constant volume, dT is rise in temperature and dV represents change in volume.

$$\text{Then, } dU = C_v dT \text{ and } dW = pdV$$

$$\Longrightarrow \quad dQ = C_v + pdV$$

From second law of thermodynamics, the change in entropy is

$$dS = dQ/T = (C_v dT)/T + pdV / T \text{ ------------ } (1)$$

If select some arbitrary state1 at temperature $T_0$, pressure $P_0$ and volume $v_0$ in which the entropy of the gas is change in entropy during state1 to state2 at temperature T, pressure P and volume V is given by,

$$\Delta s = s - s_0 = \int_1^2 \frac{C_v dT}{T} + \int_1^2 \frac{P\, dV}{T} \quad \text{------------ (2)}$$

(a) Value of S terms of temperature and volume

From the equation of state of an ideal gas

$$PV = nRT$$

$$\Longrightarrow P = nRT / V$$

Sub. value of P in eqn (2).

$$\Delta S = \int_1^2 \frac{C_v dT}{T} + nR \int_1^2 \frac{dV.T}{V.T} \quad \text{------------- (3)}$$

If Cv be assumed to constant, equ.

$$\Delta S = Cv\, log_e\, T/T_0 + nR\, log_e\, V/V_0 \quad \text{(state 1 and 2)} \quad \text{--------------- (4)}$$

For a case of isothermal expansion, $T = T_0$

∴ The change in entropy of gas in the case becomes

$$\Delta S = nR\, log_e \frac{V}{V_0} \quad \text{--------------- (5)}$$

*(b) Value of S in terms of temperature and pressure:*

$$PV = nRT$$

$$V = nRT/P$$

$$\text{and } PdV + VdP = nRdT \quad \text{-------- (5a)}$$

$$\text{So that } PdV = nRdT - VdP = nRdT - \frac{nRT dP}{P} \text{ using (5a)}$$

Sub. the value PdV in eq. (2)

$$\Delta S = \int_1^2 Cv \frac{dT}{T} + nR \int_1^2 \left(\frac{dT}{T} - \frac{dP}{P}\right)$$

$$= C_V \log_e \frac{T}{To} + nR\left(\log_e \frac{T}{To} - \log_e \frac{P}{Po}\right)$$

For an ideal gas, $C_P - C_V = nR$

$$\Delta S = C_P \log_e \frac{T}{To} + (C_P - C_V) \log_e \frac{P}{Po}$$

For isothermal change $T=T_0$, therefore change in entropy of the gas,

$$\Delta S = (C_P - C_V) \log_e \frac{P}{Po} = nR \log_e \frac{P}{Po} \qquad \text{----------} (7)$$

*(c) Value of S in terms of pressure and volume*

$$PV = nRT$$

So that, $T = \frac{PV}{nR}$ and $dT = \frac{PdV + VdP}{nR}$

Sub. these value in equ. 2,

$$\Delta S = \int_1^2 Cv \frac{PdV + VdP}{dV} + nR \int_1^2 \frac{PdV}{PV}$$

$$= \int_1^2 Cv\left(\frac{dV}{V} + \frac{dP}{P}\right) + (Cp - Cv) \int_1^2 \frac{dV}{V}$$

$$= \int_1^2 \left(Cv \frac{dP}{P} + Cp \frac{dV}{V}\right)$$

$$\Delta S = Cv \log_e P/Po + C_P \log_e V/Vo \qquad \text{-----------} (8)$$

(ii) Entropy of steam

Let consider mass m of ice at absolute temp. $T_1$, find the total gain in entropy when ice changes into steam at absolute temperature $T_2$.

If small amount of heat dQ is given to a substance at temperature T, the change in entropy is dS =dQ/T.

To convert mass m of ice at $T_1$K into water at same temperature, the amount of heat required = $mL_i$, where $L_i$ is the latent heat of ice.

Change in entropy during this process = $mL_i/T$ -------- (i)

When mass m of water at $T_1$ K is heated to $T_2$ K, the change in entropy,

$$\Delta S = \int_{T1}^{T2} \frac{dQ}{T} = \int_{T1}^{T2} \frac{mCdT}{T} = mC\ \log_c T_2/T_1 \qquad \text{-------- (ii)}$$

To convert mass m of water at $T_2$C into steam at same temperature, the amount of heat required = $mL_s$, where $L_s$ is latent heat of steam.

Change in entropy during this process = $mL_s/T_2$ ------- (iii)

Total gain in entropy = $\frac{mLi}{T1} + mCloge\left(\frac{T2}{T1}\right) + mL_s/T_2$

## PRINCIPLE OF INCREASE OF ENERGY OR DEGRADATION OF ENERGY

The entropy of a system remains constant in reversible cyclic process but increased inevitably in all irreversible process. Since a reversible process represents a limiting ideal case, all actual process are inherently irreversible. It means that as cycle after cycle of operation is performed, the entropy of the system increase and tends to a maximum value. This is the principal of increase of entropy and may be stated as " The entropy of an isolated or self contained system either increase or remains constant according as the process it undergoes are irreversible or reversible". Analytically it may be expressed as greater than 0; where the equality sign refers to reversible processes and the inequality sign to irreversible processes. Therefore the necessary and sufficient conditions of equal brim of a self contained system is that it's entropy should be maximum and it cannot be greater than zero.

Since all physical operation in the universe are irreversible for every such operations performed, a certain amount of energy become unavailable for useful work and is added to the universe in the form of heat through friction, conduction or radiation. In this way in a distant future on account of irreversibly all energies existing in different forms will be converted into heat energy and will not be available for conversion into mechanical work i.e " The available energy of the universe is tending toward zero " it will correspond to a state of maximum entropy and all temperature difference between various bodies of the universe will be equalized due to convection etc. No heat engine will then be able to work in this state because no heat flow would be possible due to the uniformity of the temperature throughout the universe .This is called the principal of degradation of energy is conserved it is transformed into a form which is unavailable for work . Thus the energy is "running down hill" and the universe is marching toward stage of die a "head - death".

With an increase in entropy, the thermal agitation and hence disorder of molecules of a substance increase, i.e increase of entropy implies a transition from order to discord. Thus the principal of increase of entropy is intimately connected with the less ordered state of affairs. According to it, a system posing high entropy should be in great disorder or chaos. Thus the entropy of a substance in gaseous state is more than in liquid state, because the molecules are free to move about in great disorder in a gas than in a liquid. Moreover the entropy is more in a liquid state than in the solid state, as the molecules are more free to move in a liquid than in a solid. Hence when ice is converted into water and then into steam, the entropy and disorder of molecules increase. On the other hand when the steam is converted into water and then in to ice, the entropy and disorder of molecules continually decreased. Thus when the temperature of a system is decreased, the amount of entropy and disorder in it decreased. Entropy of the substance is therefore said to be a measure of the degree of disorder prevailing among it's molecules just as the temperature is a measure of the degree of hotness of a substance at the absolute zero of temperature the thermal motion completely disappears so that the disorder and hence the entropy tends to zero and the molecules of a substance are in perfect order i.e well arranged.

By summarizing the above arguments, say that the entropy of any isolated system increase and approaches more or less rapidly to the inert state of maximum entropy. We may recognize this fundamental law of physics to be an inherent tendency of nature to be processed from a more ordered state to a less ordered one or from a less disordered to a more disordered state or other words that the ultimate destiny of universe is not order but chaos.

## THERMODYNAMIC POTENTIALS:

The thermodynamics variables such as pressure P, Volume V, temperature T and entropy S, define the stole of thermo dynamical system. A relation b/n them exists because of the two thermodynamic laws.

$$dQ = dU+PdV$$

$$dQ = TdS$$

Combining

$$TdS = dU + PdV$$

$$dU = TdS - PdV$$

Any two of above variables are independent and with the help of above relation remaining variables be determined. These relations are termed as thermodynamic potentials of thermodynamic fn.

## Enthalpy or Heat content H

Thermodynamical phenomena at constant pressure are expressed in terms of another function called enthalpy or heat content of the system.

$$H = U + PV \qquad \text{---- (1)}$$

diff. $dH = dU + PdV + VdP$

$$= (TdS - PdV) + PdV + VdP$$

$$= TdS + VdP$$

$$dH = Tds \qquad \text{------ (2)}$$

because process is carried at constant pressure. Since Tds = dQ, we find dH=dQ enthalpy represents the quantity of heat given to the system from an external source & hence the name heat content.

Let $H_i$ and $H_f$ be the initial and final enthalpy,

$$H_f - H_i = Q$$

The change in enthalpy during an isobaric process equal too the heat transferred.

H has an important property in porous plug exp let $P_i$ and $V_i$ be the initial pressure & volume of a gas before passing through porous plug. Similarly pf and vf be the similar quantities of the gas after passing thro' the porous plug.

External work done by gas = $P_fV_f-P_iV_i$

This work done at the cost of internal energy of the because no heat exchanges b/n gas and surrounding, suppose Ui and Uf be the initial and final internal energy.

$$U_i - U_f = P_f V_f - P_i V_i$$

$$U_i + P_iV_i = P_f V_f + U_f$$

$$\text{(or)}\ \ H_i = H_f$$

Thus in throttling process, the initial and final enthalpy remain same.

Taking partial diff. of H w.r.t. to independent variables S and P,

$$\Rightarrow \quad \left(\frac{\partial H}{\partial P}\right)_S = V \text{ and } \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{------ (3)}$$

As dH is perfect diff.

$$\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)$$

Using (3), we get

$$\left(\frac{\partial V}{\partial P}\right)_V = \left(\frac{\partial T}{\partial P}\right)_S \qquad \text{------- (4)}$$

Which is third thermodynamical relation.

**Helmholtz Function F**

On combining I & II law of thermodynamics,

dU = Tds – dW

suppose the temp of the system remain constant, then

d(TS) = Tds

$\Rightarrow$ dU=d(TS)-dW

d(U-TS) = –dW

where the fn. F=U-TS

⇨ dF=-dW --------- (1)

is called Helmholtz fn. Or Helmholtz free energy, which represents that in revisable isotheral process, the work done by the system is equal to decrease in Helmholtz Fn. F is also called as work fn.

on diff. Eqn. (1), we pet

dF=dU-TdS-SdT

sub. dU=TdS-PdV

⇨ dF=TdS-PdV-TdS-SdT

= -PdV-SdT - (2)

On partial diff. Of F w.r.to independent variables T & V.

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \text{------- (3)}$$

As dF is a perfect diff,

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial V}\right)$$

using eq. (3) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This eqn. given a relation b/n 4 thermo dynamical variable P,V,S and T. This is second thermodynamical relation

**Gibbs potential (G)**

If thermodynamic process is isothermal and isobaric (dp=0) then from qn.(2) we get

$$dH = T(ds)$$

$$= d\,(TS) \quad \text{[from Helmholtz fn.]}$$

$$d(H-TS) = 0$$

$$dG = 0$$

$$\text{Where } G = H - TS$$

$$G = U+PV-TS$$

is called gibb's fn. or free energy. On diff. (5), we get

$$dG = dU+PdV+VdP - TdS - SdT$$

$$= (\cancel{TdS} - \cancel{pdV}) + \cancel{pdV} + VdP - \cancel{TdS} - SdT$$

$$dG = VdP - SdT \qquad \text{----- (6)}$$

Talking partial derivatives of a w.r. to independent variable P and T, we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{------- (7)}$$

As dG is perfect diff ., $\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)$

This is called fourth thermodynamical relation.

**PHASE TRANSITIONS**

Simple substances are capable of existing in phases of three types: solid, liquid and gas. The three lines, in phase diagram separating these planes are called phase equilibrium lines. The common point A where three lines meet is called *triple point*; at this unique temperature and pressure all three phases can coexist in equilibrium with each other. Point C is the critical point at which liquid gas equilibrium line ends. The volume change ΔV between liquid and gas then approached zero; beyond C there is no further phase transition since only one fluid phase exist.

## CLASUSIS CLAYPERON EQUATION

Maxwell second thermo dynamical relation is

$$\left(\frac{\partial S}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

Multiply both sides by T,

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

From II law of thermodynamics,

$$TdS = dQ$$

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$\left(\frac{\partial Q}{\partial V}\right)_T$ represent the quantity of heat absorbed or liberated per unit charge in volume at constant temp. This means that at constant temp. The heat absorbed or liberated bring out simply a change in the volume of the substance. Therefore this amount of heat absorbed or liberated at constant temp must be the latent heat and change in volume must be due to change of state. Considering a unit mass of the substance let L be the latent heat when the substance change in volume from $V_1$ to $V_2$ at constant temp. then,

$$\delta Q = L \text{ and } \delta V = V_2 - V_1$$

$$\left(\frac{L}{V_2 - V_1}\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{L}{V_2 - V_1} = T\frac{\partial P}{\partial T}$$

$$dP/\,dT = \frac{L}{T(V_2 - V_1)}$$

which is called Clausius Clapyeron latest heat equation.

## VAN DER WAAL'S EQUATION OF STATE

Consider the volume occupied by the gas molecules negligible compared with the total volume of gas and the molecules exert no appreciable forces on one another. It is evident that both these assumptions cannot be exactly true for actual gases particularly at high pressure. In driving van der waals eqn. Of state the effect both these factor is taken into account.

Due to the finite size of molecules, the free space available for their movement is less than the actual measured volume of the gas. Also the number of collisions with the walls of containing vessel, and the pressure will be greater than the calculated by simple theory. The actual volume can be brought about by subtracting a career term b from the measured volume and using (v-b) in place of V in ideal gas equation.

Let XY be the portion of boundary wall. Consider a molecule A in the interior far from the boundary wall. It is surrounded by other molecules equally distributed in all directions. Those molecules exert attractive force on molecule A, when averaged out , over a sufficient interval of time they cancel out and net cohesion force will be zero. On the other hand the molecule B is as rear the boundary as it can go. In this case the molecular distribution is only along one side. The adhesive force between the gas molecules and the boundary walls are always must smaller than the cohesive force, between the gas molecules. The force on B due to each adjacent molecule can be resolved into components to the boundary wall. The parallel components cancel out on the average but the perpendicular components will result a field of force acting inwards on the molecules near the boundary wall. Thus whenever a molecule will strike the walls of the containing vessel at B to contribute its share towards the total gas pressure, the measured pressure P is loss than the ideal pressure calculate on the assumption that the cohesive force is P, the add a correction term P, to the measured pressure P and use $(P+P_1)$ in place of P in ideal gas.

On using both corrections in ideal gas equation, we get for a gram molecule of a gas.

$$(P+P_1)(V-b) = RT \qquad (1)$$

The value of $P_1$ is to the number of molecules striking in area of the wall in unit time & to the intensity of the field of force. Both of these factors are proportional to the density of the gas.

$$p_1=a\rho^2$$

$$C\text{->constant}$$

$$\rho \ \alpha \ 1/V$$

Hence $p_1=a/V^2$, where a is constant.

Sub. this value of $p_1$, in equation (1),

$$(p+a/V^2)(v-b)=RT \qquad \rightarrow(2)$$

This is van der waal's equation of state. This is the simplest and the most well known equation of stove for real gas.

Another useful form of the equation of state of a real gas is

$$PV=A+B/V+C/V^2+\ldots\ldots \qquad \rightarrow(3)$$

A,B,C,... are from of temp and are called virial coeff.

For an ideal gas it is evident that A=RT and all other viral coeff. are zero.

Van der walls equation can be but in virial form as,

Equation (2) rewritten as,

$$1=RT/((P+a/V^2)(v-b))$$

(or) $$PV=RT(l-a/PV^2)^{-1}\ (l-b/v)^{-1} \qquad \rightarrow(4)$$

The correction terms $a/PV^2$ & b/V are both small composed with unity provided the gas is not too much compressed. Using binomial theorem & neglecting the terms of higher power a l/V, equation V1, becomes,

$$PV=RT(l-A/PV^2)\ (l+B/V)+b^2/v^2$$

$$=RT-RT/PV.a/v+RT.b/v+RTb^2/v^2$$

Since PV=RT approx,

$$PV=RT+(RTb-a)/v+RTb^2/v^2 \quad \rightarrow (5)$$

This is van der waal's equation in virial form having only three virial coeff., A,B,&C

$$A=RT,\ B=RTb-a,\ C=RTb^2$$

**Possible Questions**

1. Define entropy.
2. State first and second law of thermodynamics.
3. What are called thermodynamic potentials?
4. Define the term drift variation and collision interaction.
5. Write down the Clausius-Clapeyron equation for latent heat.
6. Distinguish between real and ideal gas.
7. State third law of thermodynamics.
8. Define Helmholtz function.
9. Calculate the entropy change in reversible processes.
10. Derive Vander Waals equation of state.
11. Derive Clausius-Clapeyron equation.
12. Obtain Helmholtz free energy Gibbs function.
13. Define the term “phase transition”.
14. Obtain three different thermodynamic potentials.
15. Explain principle of increase of entropy.

Enable | Enlighten | Enrich
KARPAGAM
ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956 )

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**
**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT I (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | The term “thermodynamics” comes from Greek. words “therme” and “dynamis” which means _______. | Heat power | Heat transfer | Heat energy | Heat motion | Heat power |
| 2 | The term “thermodynamics” was first used in 1849 in the publication of a | Rudolph Clausius | William Rankine | Lord Kelvin | Thomas Savery | Lord Kelvin |
| 3 | The macroscopic approach to the study of thermodynamics does not require a knowledge of the behavior of individual particles is called _____. | Dynamic thermodynamics | Static thermodynamics | Statistical thermodynamics | Classical thermodynamics | Classical thermodynamics |
| 4 | What law asserts that energy is a thermodynamic property? | First law of Thermodynamics | Second law of Thermodynamics | Third law of Thermodynamics | Zeroth law of Thermodynamics | First law of Thermodynamics |
| 5 | What law asserts that energy has quality as well as quantity? | First law of Thermodynamics | Second law of Thermodynamics | Third law of Thermodynamics | Zeroth law of Thermodynamics | Second law of Thermodynamics |
| 6 | The first law of thermodynamics is based on which of the following principles? | mass of energy | Conservation of energy | Conservation of MOMENTUM | The entropy-temperature relationship | Conservation of energy |
| 7 | Thermodynamics is applicable to | microscopic systems only | macroscopic systems only | homogeneous systems only | heterogeneous systems only. | macroscopic systems only |
| 8 | Which is not true about thermodynamics ? | it ignores the | it involves the | it is concerned | it is not | it is not applicable |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | internal structure of atoms and molecules | matter in bulk | only with the initial and final states of the system | applicable to macroscopic systems. | to macroscopic systems. |
| 9 | A system that can transfer neither matter nor energy to and from its surroundings is called | closed system | an isolated system | an open system | a homogeneous system | an isolated system |
| 10 | Which of the following is incorrect, for an ideal gas ? | PV= nRT | V= nRT/P | P=nRT/V | P =RT | PV= nRT |
| 11 | The heat capacity at constant pressure is related to heat capacity at constant volume by the relation | Cp-R =Cv | Cv-R =Cp | Cp-Cv =R | R-Cp =Cv | Cp-Cv =R |
| 12 | A system is in ______ equilibrium if the temperature is the same throughout the entire system. | Static | Thermal | Mechanical | Phase | Thermal |
| 13 | A system is in ______ equilibrium if there is no change in pressure at any point of the system with time. | Pressure | Thermal | Mechanical | Phase | Mechanical |
| 14 | If a system involves two phases, it is in ______ equilibrium when the mass of each phase reaches an equilibrium level and stays there. | Chemical | Thermal | Mechanical | phase | Phase |
| 15 | A system is in ______ equilibrium of its chemical composition does not change with time, i.e., no chemical reaction occurs. | Chemical | Thermal | Mechanical | Phase | Chemical |
| 16 | A system is said to be in thermodynamic equilibrium if it maintains ______ equilibrium. | Mechanical and phase | Thermal and chemical | Thermal, mechanical and chemical | Thermal, phase, mechanical and chemical | Thermal, phase, mechanical and chemical |
| 17 | What is a process with identical end states called? | Cycle | Path | Phase | Either path or phase | Cycle |
| 18 | What is a process during which the temperature remains constant? | Isobaric process | Isothermal process | Isochoric process | Isometric process | Isothermal process |
| 19 | What is a process during which the pressure remains constant? | Isobaric process | Isothermal process | Isochoric process | Isometric process | Isobaric process |

| | | | | | | |
|---|---|---|---|---|---|---|
| 20 | What is a process during which the specific volume remains constant? | Isobaric process | Isothermal process | Isochoric or isometric process | Isovolumetric process | Isochoric or isometric process |
| 21 | What states that if two bodies are in thermal equilibrium with a third body, they are also in equilibrium with each other? | Zeroth law of thermodynamics | First law of thermodynamics | Second law of thermodynamics | Third law of thermodynamics | Zeroth law of thermodynamics |
| 22 | What is the study of energy and its transformations? | Thermostatics | Thermophysics | Thermochemistry | Thermodynamics | Thermodynamics |
| 23 | What is considered as the heat content of a system? | Enthalpy | Entropy | Internal heat | Molar heat | Enthalpy |
| 24 | What refers to the amount of heat needed to raise the temperature of an object by one degree Celsius or 1K? | Heat capacity | Specific heat | Latent heat | Molar heat | Heat capacity |
| 25 | What is the heat capacity of one mole of substance? | Molecular heat | Specific heat | Latent heat | Molar heat | Specific heat |
| 26 | What refers to the measure of the disorder present in a given substance or system? | Enthalpy | Entropy | Heat capacity | Molar heat | Entropy |
| 27 | Entropy is measured in ______. | Joule/Kelvin | Joule-Meter/Kelvin | Meter/Kelvin | Newton/Kelvin | Joule/Kelvin |
| 28 | What is the energy absorbed during chemical reaction under constant volume conditions? | Entropy | Ion exchange | Enthalpy | Enthalpy of reaction | Enthalpy |
| 29 | Which of the following equation is used to calculate the heats of reaction when ΔG at two temperatutes are given? | Gibbs Helmholtz equatioin | Clapeyron equation | Kirchoffs equation | Nernst equation | Gibbs Helmholtz equatioin |
| 30 | ____________ is applicable to macroscopic systems only. | thermochemistry | thermokinetics | thermodynamics | thermochemical studies. | thermodynamics |
| 31 | ΔE =q-w for an isochoric process | first law of thermodynamics | second law of thermodynamics | zeroth's law | third law of thermodynamics | first law of thermodynamics |
| 32 | Who proposed the Carnot cycle? | Sammy Carnot | Sonny Carnot | Sadi Carnot | Suri Carnot | Sadi Carnot |
| 33 | Entropy is transferred by ______. | Work | Heat | Energy | Work and heat | Heat |
| 34 | Gibb's function is expressed as, | G = H + TS | G = H / TS | G=H-TS | G = H * TS | G=H-TS |
| 35 | Average kinetic energy of molecules is | Directly proportional to | Directly proportional to | Independent of absolute | Inversely proportional to | Directly proportional to |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | square root of temperature | absolute temperature | temperature | absolute temperature | absolute temperature |
| 36 | The specific heat of a gas in isothermal process is | Zero | Negative | Remains constant | Infinite | Infinite |
| 37 | Latent heat of ice is | Less than external latent heat of fusion | Equal to external latent heat of fusion | More then external latent heat of fusion | Twice the external latent heat of fusion | Twice the external latent heat of fusion |
| 38 | The difference between the principal specific heats of nitrogen is 300 J/kg °K and ratio of the two specific heats is 1.4. then the CP is | 1050 J/kg °K | 650 J/kg °K | 750 J/kg °K | 150 J/kg °K | 650 J/kg °K |
| 39 | The mean kinetic energy of one gram-mole of a perfect gas at absolute temperature T is | 1/2 KT | 1/2 RT | 3/2 KT | 3/2 RT | 3/2 RT |
| 40 | The specific heat of a substance at its boiling point or melting point | Is zero | Is infinity | Is negative | Lies between 0 and 1 | Is infinity |
| 41 | Which of the following variables controls the physical properties of a perfect gas? | Pressure | Temperature | Volume | Atomic mass | Atomic mass |
| 42 | A system in which state variables have constant values throughout the system is called in a state of | equilibrium | non- equilibrium | isothermal equilibrium | none of these. | equilibrium |
| 43 | In an adiabatic process ______ can flow in to or out of the system. | no heat | heat | matter | no matter.. | no heat |
| 44 | The mathematical relation for the first law of thermodynamics is | $\Delta E = q + w$ | $\Delta E = 0$ for a cyclic process | $\Delta E = -q$ for an isochoric process | $\Delta E = W - q$. | $\Delta E = q + w$ |
| 45 | For an adiabatic process according to first law of thermodynamics, | $\Delta E = -w$ | $\Delta E = w$ | $\Delta E = q - w$ | $\Delta q = E - w$ | $\Delta E = -w$ |
| 46 | The enthalpy change, $\Delta H$ of a process is given by the relation | $\Delta H = \Delta E + p\Delta v$ | $\Delta H = \Delta E + \Delta nRT$ | $\Delta H = \Delta E + w$ | $\Delta H = \Delta E - \Delta nRT$ | $\Delta H = \Delta E + p\Delta v$ |
| 47 | The amount of heat required to raise the temperature of one mole of the substance by 1 K is called | heat capacity | molar heat capacity | molar heat | molar capacity. | molar heat capacity |
| 48 | Which of the following is not correct ? | $H=E+PV$ | $H-E=PV$ | $H-E-PV=0$ | $H=E-PV$ | $H=E-PV$ |
| 49 | The enthalpy of a system is defined by the relation | $H=E+PV$ | $H=E-Pv$ | $E=H+PV$ | $PV+E-H$ | $H=E+PV$ |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 50 | Which of the following law is applicable for the behavior of a perfect gas | Boyle’s law | Charles law | Gay-lussac law | Joules law | Joules law |
| 51 | An ideal gas as compared to a real gas at very high pressure occupies | More volume | Less volume | Same volume | Unpredictable behavior | More volume |
| 52 | The unit of pressure in SI unit is | Kg/cm2 | Mm of water column | Pascal | Bars | Pascal |
| 53 | Temperature of a gas is produced due to | Its heating value | Kinetic energy of molecules | Repulsion of molecules | Surface tension of molecules | Kinetic energy of molecules |
| 54 | According to kinetic theory of gases, the absolute zero temperature is attained when | Volume of the gas is zero | Pressure of the gas is zero | Kinetic energy of the molecules is zero | Mass is zero | Kinetic energy of the molecules is zero |
| 55 | Kinetic theory of gases assumes that the collisions between the molecules are | Perfectly elastic | Perfectly inelastic | Partly elastic | Partly inelastic | Perfectly elastic |
| 56 | The behavior of gases can be fully determined by | 1 law | 2 law | 3 law | 4 law | 4 law |
| 57 | Boyle’s law ie, PV = constant is applicable to gases under | All ranges of pressures | Only small range of pressures | Steady change of pressures | Atmospheric conditions | Only small range of pressures |
| 58 | The same volume of all gases would represent their | Densities | Specific weights | Molecular weights | Gas characteristic constants | Molecular weights |
| 59 | Gases have | Only one value of specific heat | Two value of specific heat | Three value of specific heat | No value of specific heat | No value of specific heat |
| 60 | Which of the following quantities is not the property of the system | Pressure | temperature | heat | density | density |

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**

**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT II (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | Which of the following statements is TRUE for an ideal gas, but not for a real gas? | PV = nRT | An increase in temperature causes an increase in the kinetic energy of the gas | The total volume of molecules on a gas is nearly the same as the volume of the gas as a whole | No attractive forces exists between the molecule of a gas | PV = nRT |
| 2 | The molecules of a gas moving through space with some velocity possesses what kind of energy? | Translational energy | Spin energy | Rotational kinetic energy | Sensible energy | Translational energy |
| 3 | Molar specific heat at constant volume is $C_v$ for a monoatomic gas is. | 3/2 R | 5/2 R | 3R | 2R | 3/2 R |
| 4 | If the pressure in a closed vessel is reduced by drawing out some gas, the mean free path of the molecules. | Is decreased | Remains unchanged | Is increased | Increases or decreases according to the nature of the gas | Is increased |
| 5 | Cooking gas containers are kept in a lorry moving with uniform speed. The temperature of the gas molecules inside | Increase | Remain same | Decrease | Decrease for some, while increase for | Remain same |

| | | | | | | |
|---|---|---|---|---|---|---|
| | will. | | | | others | |
| 6 | Volume of gas become four times if. | Temperature become four times at constant pressure | Temperature becomes two times at constant pressure | Temperature become one fourth at constant pressure | Temperature becomes half at constant pressure | Temperature become four times at constant pressure |
| 7 | Molecules of a gas behave like. | Inelastic rigid sphere | Perfectly elastic rigid sphere | Perfectly elastic non-rigid sphere | Inelastic non-rigid sphere | Perfectly elastic rigid sphere |
| 8 | At absolute zero temperature, pressure of a gas will be | Zero | Po * 273 | One atmospheric pressure | Po * 76 | Zero |
| 9 | Boyle's law holds for an ideal gas during | Isobaric changes | Isochoric changes | Isothermal changes | Isotonic changes | Isothermal changes |
| 10 | Kinetic theory of gases provide a base for | Charle’s law | Charle’s law and Boyle’s law | Boyle’s law | stefans law | Charle’s law and Boyle’s law |
| 11 | In Boyle's law what remains constant. | PV | TV | V/T | V/T | PV |
| 12 | S.I. unit of universal gas constant is | cal/°C | J/molK | J/mol | J/kg | J/molK |
| 13 | At constant volume, temperature is increased. Then. | Collision on walls will be less | Collisions will be in straight lines | Number of collisions per unit time will increase | Collisions will not change | Number of collisions per unit time will increase |
| 14 | The specific heat of a gas | Has only two values Cp and Cv | Can have any value between 0 and ∞ | Has a unique value at a given temperature | Depends upon the mass of the gas | Has only two values Cp and Cv |
| 15 | For Boyle's law to hold the gas should be. | Perfect and of constant mass and temperature | Perfect and at constant temperature but variable mass | Real and of constant mass and temperature | Real and at constant temperature but variable mass | Perfect and of constant mass and temperature |
| 16 | Every gas (real gas) behaves as an ideal gas. | At high temperature and low pressure | At normal temperature and pressure | At low temperature and high pressure | low pressure | At high temperature and low pressure |
| 17 | According to kinetic theory of gasses at | Water freezes | Liquid helium | Molecules | Liquid | Molecules motion stops |

| | | | | | | |
|---|---|---|---|---|---|---|
| | absolute zero temperature | | freezes | motion stops | hydrogen freezes | |
| 18 | For an ideal gas Cp and Cv is | grater than one | less than one | equal to one | not equal to one | less than one |
| 19 | An ideal gas is that which can | Be solidified | Liquefied | Not be liquefied | Not be solidified | Not be liquefied |
| 20 | Average kinetic energy of molecules is | Directly proportional to square root of temperature | Directly proportional to absolute temperature | Independent of absolute temperature | Inversely proportional to absolute temperature | Directly proportional to absolute temperature |
| 21 | Latent heat of ice is | Less than external latent heat of fusion | Equal to external latent heat of fusion | More then external latent heat of fusion | Twice the external latent heat of fusion | More then external latent heat of fusion |
| 22 | The specific heat of a substance at its boiling point or melting point | Is zero | Is infinity | Is negative | Lies between 0 and 1 | Is infinity |
| 23 | Which of the following properties of gas molecule the one that is same for all ideal gases at a particular temperature is | Mass | velocity | momentum | kinetic energy | Mass |
| 24 | Mean kinetic energy of perfect gas is | Proportional to T | Inverse proportional to $T^{2}$ | Inverse proportional to $T^{-2}$ | Inverse proportional to $T^{1/2}$ | Proportional to T |
| 25 | The motion of fluids and the forces acting on solid bodies immersed in fluids and in motion relative to them is called | dynamics | hydrodynamics | statitics | mechanics | hydrodynamics |
| 26 | Temperature of a gas can be related to the …………….motion of the molecules | external | boundary | internal | closed | internal |
| 27 | Boltzmann's constant is | 1.38 x 10-23 j/k | 1.38 x 10-31 j/k | 1.38 x 10-32 j/k | 1.38 x 10-19 j/k | 1.38 x 10-23 j/k |
| 28 | The word kinetic refers to | locomotion | vibration | motion | resonance | motion |

| | | | | | | |
|---|---|---|---|---|---|---|
| 29 | In gases the particles are | closely packed | not free to move | regularly packed | far apart | far apart |
| 30 | Gases have | low density and mass | high density and mass | high density but low mass | low density but high mass | low density and mass |
| 31 | what does the Kinetic theory of gases describe? | small no of small particles in constant randam motion | large no of small particles in constant randam motion | large no of small particles in accelerating randam motion | large no of large particles in constant randam motion | large no of small particles in constant randam motion |
| 32 | which experiment shows how kinetic theory works? | g by freefall | brownian motion | pin hole camera | refration of light | brownian motion |
| 33 | what forces are assumed to exist between particles in a gas | attractive | repulsive | both | no force | no force |
| 34 | Kinetic is a / an | latin word | roman word | greek word | arabic word | greek word |
| 35 | Which one of the following have the highest volume? | solid | Liquid helium freezes | gas | Gel | gas |
| 36 | Gases are | very compressible | very little compressible | incompressible | not possible | very compressible |
| 37 | The three states of matter depend on | Temperature become four times at constant pressure | force | potential energy | biomass | Temperature |
| 38 | The term fluids is used for | liquid only | gases only | liquid and gass | gel only | liquid and gas |
| 39 | Why are liquids and gases termed as fluids? Because | they can flow | they have irregular shape | they have randomly moving | they are compressible | they can flow |
| 40 | The Brownian Motion was discovered by the scientist | albert brown | John brown | robert brown | issac brown | John brown |
| 41 | If the car tires are hot, the pressure of gas molecules in them would be | high | low | same as before heating | may be high or low | high |
| 42 | Gas can exert | pressure on wall | force on the base | pressure in solid | force in liquid | pressure on wall |

| | | | | | | |
|---|---|---|---|---|---|---|
| 43 | The random motion of smoke or gas particles in the air is termed as | brueian motion | brownian motion | radom motion | static | brownian motion |
| 44 | All of the following are basic assumptions of the kinetic theory except: | matter is composed of very tiny particles | when individual particles collide, they undergo no exchange of kinetic energy | the total kinetic energy of colliding particles remains constant | the particles of matter are in continual motion | when individual particles collide, they undergo no exchange of kinetic energy |
| 45 | For a gas, which pair of variables are inversely proportional to each other (if all other conditions remain constant)? | P,T | P,V | V,T | n,V | P,T |
| 46 | The behavior of gases can be fully determined by | 1 law | 2 law | 3 law | 4 law | 4 law |
| 47 | Solid and liquids have | Only one value of specific heat | Two value of specific heat | Three value of specific heat | No value of specific heat | Only one value of specific heat |
| 48 | The term N.T.P stands for | Nominal temperature and pressurre | Natural temperature and pressure | Normal temperatuere and pressure | Normal thermodynamic pressure | Normal temperatuere and pressure |
| 49 | Boyle’s law ie, PV = constant is applicable to gases under | All ranges of pressures | Only small range of pressures | Steady change of pressures | Atmospheric conditions | Only small range of pressures |
| 50 | The term N.T.P stands for | Nominal temperature and pressure | Natural temperature and pressure | Normal temperature and pressure | Normal thermodynamic pressure | Normal temperature and pressure |
| 51 | M.B. distribution can be applicable to __________ | identical molecule | indistinguishable molecule | gas | liquid | identical molecule |

Enable | Enlighten | Enrich
KARPAGAM
ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956)

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**
**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT II (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | Which of the following statements is TRUE for an ideal gas, but not for a real gas? | PV = nRT | An increase in temperature causes an increase in the kinetic energy of the gas | The total volume of molecules on a gas is nearly the same as the volume of the gas as a whole | No attractive forces exists between the molecule of a gas | PV = nRT |
| 2 | The molecules of a gas moving through space with some velocity possesses what kind of energy? | Translational energy | Spin energy | Rotational kinetic energy | Sensible energy | Translational energy |
| 3 | Molar specific heat at constant volume is $C_v$ for a monoatomic gas is. | 3/2 R | 5/2 R | 3R | 2R | 3/2 R |
| 4 | If the pressure in a closed vessel is reduced by drawing out some gas, the mean free path of the molecules. | Is decreased | Remains unchanged | Is increased | Increases or decreases according to the nature of the gas | Is increased |
| 5 | Cooking gas containers are kept in a lorry moving with uniform speed. The temperature of the gas molecules inside | Increase | Remain same | Decrease | Decrease for some, while increase for | Remain same |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | will. |  |  |  | others |  |
| 6 | Volume of gas become four times if. | Temperature become four times at constant pressure | Temperature becomes two times at constant pressure | Temperature become one fourth at constant pressure | Temperature becomes half at constant pressure | Temperature become four times at constant pressure |
| 7 | Molecules of a gas behave like. | Inelastic rigid sphere | Perfectly elastic rigid sphere | Perfectly elastic non-rigid sphere | Inelastic non-rigid sphere | Perfectly elastic rigid sphere |
| 8 | At absolute zero temperature, pressure of a gas will be | Zero | Po * 273 | One atmospheric pressure | Po * 76 | Zero |
| 9 | Boyle's law holds for an ideal gas during | Isobaric changes | Isochoric changes | Isothermal changes | Isotonic changes | Isothermal changes |
| 10 | Kinetic theory of gases provide a base for | Charle’s law | Charle’s law and Boyle’s law | Boyle’s law | stefans law | Charle’s law and Boyle’s law |
| 11 | In Boyle's law what remains constant. | PV | TV | V/T | V/T | PV |
| 12 | S.I. unit of universal gas constant is | cal/°C | J/molK | J/mol | J/kg | J/molK |
| 13 | At constant volume, temperature is increased. Then. | Collision on walls will be less | Collisions will be in straight lines | Number of collisions per unit time will increase | Collisions will not change | Number of collisions per unit time will increase |
| 14 | The specific heat of a gas | Has only two values Cp and Cv | Can have any value between 0 and ∞ | Has a unique value at a given temperature | Depends upon the mass of the gas | Has only two values Cp and Cv |
| 15 | For Boyle's law to hold the gas should be. | Perfect and of constant mass and temperature | Perfect and at constant temperature but variable mass | Real and of constant mass and temperature | Real and at constant temperature but variable mass | Perfect and of constant mass and temperature |
| 16 | Every gas (real gas) behaves as an ideal gas. | At high temperature and low pressure | At normal temperature and pressure | At low temperature and high pressure | low pressure | At high temperature and low pressure |
| 17 | According to kinetic theory of gasses at | Water freezes | Liquid helium | Molecules | Liquid | Molecules motion stops |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | absolute zero temperature |  | freezes | motion stops | hydrogen freezes |  |
| 18 | For an ideal gas Cp and Cv is | grater than one | less than one | equal to one | not equal to one | less than one |
| 19 | An ideal gas is that which can | Be solidified | Liquefied | Not be liquefied | Not be solidified | Not be liquefied |
| 20 | Average kinetic energy of molecules is | Directly proportional to square root of temperature | Directly proportional to absolute temperature | Independent of absolute temperature | Inversely proportional to absolute temperature | Directly proportional to absolute temperature |
| 21 | Latent heat of ice is | Less than external latent heat of fusion | Equal to external latent heat of fusion | More then external latent heat of fusion | Twice the external latent heat of fusion | More then external latent heat of fusion |
| 22 | The specific heat of a substance at its boiling point or melting point | Is zero | Is infinity | Is negative | Lies between 0 and 1 | Is infinity |
| 23 | Which of the following properties of gas molecule the one that is same for all ideal gases at a particular temperature is | Mass | velocity | momentum | kinetic energy | Mass |
| 24 | Mean kinetic energy of perfect gas is | Proportional to T | Inverse proportional to $T^2$ | Inverse proportional to $T^{-2}$ | Inverse proportional to $T^{1/2}$ | Proportional to T |
| 25 | The motion of fluids and the forces acting on solid bodies immersed in fluids and in motion relative to them is called | dynamics | hydrodynamics | statitics | mechanics | hydrodynamics |
| 26 | Temperature of a gas can be related to the …………….motion of the molecules | external | boundary | internal | closed | internal |
| 27 | Boltzmann's constant is | 1.38 x 10-23 j/k | 1.38 x 10-31 j/k | 1.38 x 10-32 j/k | 1.38 x 10-19 j/k | 1.38 x 10-23 j/k |
| 28 | The word kinetic refers to | locomotion | vibration | motion | resonance | motion |

| | | | | | | |
|---|---|---|---|---|---|---|
| 29 | In gases the particles are | closely packed | not free to move | regularly packed | far apart | far apart |
| 30 | Gases have | low density and mass | high density and mass | high density but low mass | low density but high mass | low density and mass |
| 31 | what does the Kinetic theory of gases describe? | small no of small particles in constant randam motion | large no of small particles in constant randam motion | large no of small particles in accelerating randam motion | large no of large particles in constant randam motion | large no of small particles in constant randam motion |
| 32 | which experiment shows how kinetic theory works? | g by freefall | brownian motion | pin hole camera | refration of light | brownian motion |
| 33 | what forces are assumed to exist between particles in a gas | attractive | repulsive | both | no force | no force |
| 34 | Kinetic is a / an | latin word | roman word | greek word | arabic word | greek word |
| 35 | Which one of the following have the highest volume? | solid | Liquid helium freezes | gas | Gel | gas |
| 36 | Gases are | very compressible | very little compressible | incompressible | not possible | very compressible |
| 37 | The three states of matter depend on | Temperature become four times at constant pressure | force | potential energy | biomass | Temperature |
| 38 | The term fluids is used for | liquid only | gases only | liquid and gass | gel only | liquid and gas |
| 39 | Why are liquids and gases termed as fluids? Because | they can flow | they have irregular shape | they have randomly moving | they are compressible | they can flow |
| 40 | The Brownian Motion was discovered by the scientist | albert brown | John brown | robert brown | issac brown | John brown |
| 41 | If the car tires are hot, the pressure of gas molecules in them would be | high | low | same as before heating | may be high or low | high |
| 42 | Gas can exert | pressure on wall | force on the base | pressure in solid | force in liquid | pressure on wall |

| | | | | | | |
|---|---|---|---|---|---|---|
| 43 | The random motion of smoke or gas particles in the air is termed as | brueian motion | brownian motion | radom motion | static | brownian motion |
| 44 | All of the following are basic assumptions of the kinetic theory except: | matter is composed of very tiny particles | when individual particles collide, they undergo no exchange of kinetic energy | the total kinetic energy of colliding particles remains constant | the particles of matter are in continual motion | when individual particles collide, they undergo no exchange of kinetic energy |
| 45 | For a gas, which pair of variables are inversely proportional to each other (if all other conditions remain constant)? | P,T | P,V | V,T | n,V | P,T |
| 46 | The behavior of gases can be fully determined by | 1 law | 2 law | 3 law | 4 law | 4 law |
| 47 | Solid and liquids have | Only one value of specific heat | Two value of specific heat | Three value of specific heat | No value of specific heat | Only one value of specific heat |
| 48 | The term N.T.P stands for | Nominal temperature and pressurre | Natural temperature and pressure | Normal temperatuere and pressure | Normal thermodynamic pressure | Normal temperatuere and pressure |
| 49 | Boyle's law ie, PV = constant is applicable to gases under | All ranges of pressures | Only small range of pressures | Steady change of pressures | Atmospheric conditions | Only small range of pressures |
| 50 | The term N.T.P stands for | Nominal temperature and pressure | Natural temperature and pressure | Normal temperature and pressure | Normal thermodynamic pressure | Normal temperature and pressure |
| 51 | M.B. distribution can be applicable to __________ | identical molecule | indistinguishable molecule | gas | liquid | identical molecule |

## UNIT-III

**Classical Statistical Mechanics**: Maxwell Boltzmann distribution law: Evaluation of constants - Maxwell's law of distribution of velocities - Most probable speed, Average speed, Root mean square speed - Principle of equipartition of energy - Partition function - Condition for applicability of M.B statistics - Non degenerate and degenerate systems - Maxwell velocity distribution in a given direction - Total internal energy of an ideal gas - Molar heat capacity of a gas at constant volume – Entropy - Helmholtz free energy - Pressure and equation of state of an ideal gas - Limitation of M.B method.

## Maxwell –Boltzmann Momentum Distribution Law for an Ideal Gas

The Maxwell –Boltzmann equation for distribution of energy among the molecules of an ideal gas is

$$n(E)dE=\frac{2\pi N}{(\pi KT)^{3/2}}Ee^{1/2}e^{-E/KT}dE \quad \text{--------------------(1)}$$

All the energy of the gas in the form of K E of its molecules .Therefore

$$E=\frac{1}{2}mv^2=(\frac{(mv)^2}{2m}=\frac{p^2}{2m} \quad \text{-----------------------(2)}$$

Taking differential of this eqn..

$$dE=\frac{p}{m}dp \quad \text{-----------------------(3)}$$

sub..the expression for E and dE in eq(1), the number of molecules n(p)dp whose momentum lie between p and p+dp is

$$n(p)dp=\frac{2\pi N}{(\pi KT)^{3/2}}.(\frac{p^2}{2m})^{1/2}.e^{-p2/2mKT}.(\frac{p}{m})dp$$

$$=\frac{4\pi N}{(2\pi mKT)^{3/2}}.p^2e^{-p2/2mKT}.dp \quad \text{---------------------(4)}$$

This eq. is known as Maxwell –Boltzmann law of distribution of momenta among the molecules of an Ideal Gas.

**Evaluation of constant**

The total number N of the particles in the system is given by

$$N = \Sigma_r n_r = \sum_r e^{-\alpha} g_r e^{-Er/kT}$$

$$= e^{-\alpha}\Sigma_r\, g_r e^{-Er/kT}$$

$$=A\, \Sigma_r\, g_r e^{-Er/kT} \quad \text{-------- (1)}$$

Where $A=e^{-\alpha}$

From eq. (1) $A = \frac{N}{\sum_r g_r \, e^{\frac{-Er}{kT}}}$

For continuous variation of energy of free particles of an ideal gas, $g_r$ is replaced by g(E) dE, $E_r$ is replaced by E and the sign of summation is replaced by the sign of integration.

$$A = \int_0^\infty \frac{N}{g(E)dEe^{\frac{-Er}{kT}}} \qquad \text{----------- (2)}$$

The limits of integration are taken from 0 to ∞ because energy of the particles of an ideal gas is entirely kinetic and so they can have any K.E. The value of g(E) dE for particles with no spin is given by

$$g(E)\,dE = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

The integral in eq. (2) is evaluated as follows:

$$I = \int_0^\infty g(E)\, e^{-E/kT} dE$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty E^{1/2}\, e^{-E/kT} dE$$

Let E/kT = x, then E=kTx

Therefore dE = kTdx

$$I = 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (kTx)^{\frac{1}{2}} e^{-\frac{x}{kT}} (kT) dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{1}{2}} e^{-x} dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{3}{2}-1}\, e^{-x} dx$$

The integral on the R.H.S of this equation is a gamma-function defined as

$$\int_0^\infty (x)^{n-1}\, e^{-x} dx = \Gamma\,(n)$$

Therefore $\int_0^\infty (x)^{\frac{3}{2}-1}\, e^{-x} dx = \Gamma(3/2) = ½\sqrt{\pi}$

$I = 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}}$ x ½ $\sqrt{\pi}$ $= V \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$

Sub. the value of this integral in eq. (2),

$$A = e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \qquad \text{-------- (3)}$$

The constant A i.e., $e^{-\alpha}$ is called degeneracy parameter

Taking log on both sides, $-\alpha = \log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right]$ ------------ (4)

**Maxwell –Boltzmann speed Distribution Law**

The Maxwell –Boltzmann equation for distribution of energy among the molecules of an ideal gas is

$$n(E)dE = \frac{2\pi N}{(\pi KT)^{3/2}} E^{1/2} e^{-E/KT} dE \qquad \text{----------------------(1)}$$

A classical ideal gas is defined as an assembly of non-interacting molecules, each distinguishable from the other. Therefore, the molecules have no internal degrees of freedom, all the energy of the gas in the form of kinetic Energy of the molecules.

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m(v^2_x + v^2_y + v_z^2) \qquad \text{--------------------------(2)}$$

$$dE = mvdV \qquad \text{--------------------------(3)}$$

Substitute the expression for E and dE in eq(1), the number of molecules n(v)dv whose speeds lie in between v and v + dv is given by

$$n(v)dv = \frac{2\pi N}{(\pi KT)^{3/2}} \left(\frac{1}{2}mv^2\right)^{1/2} e^{-mv2/2KT} mv\, dv$$

$$= 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} v^2 e^{-mv2/2KT} dv \qquad \text{-------------------(4)}$$

This eq. is known as the Maxwell of Maxwell –Boltsmann law of distribution speeds among the molecules of a gas .In this equation n(v) is the number of molecules per unit speed range .Therefore , the unit of n(v) is molecules /(m/sec).

*Discussion of the law:*

The curves for n(v) plotted against v at three different temperatures $T_1$,$T_2$,$T_3$ where $T_1<T_2<T_3$

From the distribution curves we get the following conclusions.

(1)At any temperature there is no molecules having zero speed.

(2) As the speed increases the no of molecules in a given speed interval $\Delta v$ increases upto a certain maximum value.

(3) As the speed further increases beyond $v_p$ , n(p) decreases exponentially towards zero. It means according to classical physical a molecules can have a infinite speed.

(4) As the temperature increases, $v_p$ increases, and the range of speed is greater .Hence the curve become broad.

(5) At the given temperature the area under the distribution curves is equal to the total number of molecules in the gas .Thus

$$N=\int_0^\infty n(v)dv$$

Since the area must be same at all the temperature, the distributive curve must flatten as the temperature rises.

**Most Probable, Average and root mean square speed**

*Most Probable speed, $v_p$:*

The most probable speed of the molecules is that speed at which the number of molecules per unit range of speed is maximum.

From the M-B distribution law for the molecular speeds the number of molecules per unit range of speed is given by

$$n\,(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{\frac{-mv^2}{2kT}} \qquad \text{---------} \ (1)$$

Taking logarithm of both sides of this equation

$$\log n(v) = \log\left[4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2}\right] + 2\log v - \frac{mv^2}{2kT}$$

by dif.this equation with the respect v,

$$\frac{1}{n(v)}\frac{dn(v)}{dv} = 0 + \frac{2}{v} - \frac{mv}{KT}$$

$$\frac{dn(v)}{dv} = -n(v)\left[\frac{mv}{kT} - \frac{2}{v}\right] \qquad \text{--------- (2)}$$

At the most probable speed $v=v_p$ the number of molecules n(v) is maximum

$$\left[\frac{dn(v)}{dv}\right]_{v_p} = 0$$

From eq. (2)

$$\frac{mv_p}{kT} - \frac{2}{v_p} = 0$$

From this eq. $v_p = \sqrt{\frac{2kT}{m}}$ ----------- (3)

$$= 1.414\sqrt{\frac{kT}{m}}$$

*Average speed:*

The number of molecules whose speeds lie between v and v+dv is n (v) dv. The total speeds of these molecules is v n (v)dv, and the total number the molecules is N. Since the molecules is distributed among all velocities from 0 to ∞, the average speed is given by

$$\tilde{v} = \frac{1}{N}\int_0^\infty v\, n(v)\, dv \qquad -----(4)$$

$$= \frac{1}{N}\int_0^\infty v\, 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{\frac{-mv2}{2kT}} dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3\, e^{\frac{-mv2}{2kT}} dv \qquad \text{----------- (5)}$$

Let $mv^2 / 2kT = x$

Then $v = \left(\frac{2kT}{m}\right)^{1/2} x^{1/2}$

$$dv = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

Sub. these values in eq. (5),

$$\tilde{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \left(\frac{2kT}{m}\right)^{3/2} x^{3/2}\, e^{-x} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

$$= 2/\sqrt{\pi} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \int_0^\infty x\, e^{-x} dx$$

$$= \left(\frac{8kT}{m}\right)^{\frac{1}{2}} \int_0^\infty x^{2-1}\, e^{-x} dx \qquad \text{----------- (6)}$$

The integral term in gamma function defined by

$$\int_0^\infty x^{n-1}\, e^{-x} dx = \Gamma\,(n)$$

$$\int_0^\infty x^{2-1}\, e^{-x} dx = \Gamma\,(2) = 1.\Gamma\,(1) = 1.1 = 1$$

$$\text{Hence, } \tilde{v} = \sqrt{\frac{8kT}{\pi m}} \qquad \text{-------- (7)}$$

$$= 1.596 \sqrt{\frac{kT}{m}}$$

*Root mean square*

The number of molecules whose speed is between ν and ν + dν is n (ν) dν. The sum of the squares of the speeds of these molecules is $\nu^2$ n (ν) dν, and the total number of molecules is N. Since the total number of molecules is distributed among all these from 0 to ∞, the mean square speed is given by

$$\tilde{v}^2 = \frac{1}{N} \int_0^\infty v\, n\,(v)\, dv \qquad \text{--------- (8)}$$

$$= \frac{1}{N}\int_0^\infty v^2\; 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{\frac{-mv2}{2kT}}\, dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4\, e^{\frac{-mv2}{2kT}}\, dv \qquad \text{----------- (9)}$$

Let $mv^2 / 2kT = x$

Then $$v = \left(\frac{2kT}{m}\right)^{1/2} x^{1/2}$$

$$dv = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

Sub. these values in eq. (5),

$$\tilde{v}^2 = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \left(\frac{2kT}{m}\right)^2 x^2\, e^{-x} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

$$= \frac{4}{\sqrt{\pi}} \left(\frac{kT}{m}\right) \int_0^\infty x^{\frac{5}{2}-1}\, e^{-x}\, dx \qquad \text{----------- (10)}$$

The integral term in gamma function defined by

$$\int_0^\infty x^{\frac{5}{2}-1}\, e^{-x}\, dx = \Gamma(5/2) = 3/2 \times ½ \times \sqrt{\pi} = \frac{3\sqrt{\pi}}{4}$$

$$\text{Hence, } \tilde{v}^2 = \frac{4}{\sqrt{\pi}} \left(\frac{kT}{m}\right) \frac{3\sqrt{\pi}}{4} = \frac{3kT}{m}$$

$$v_{rms= \sqrt{\tilde{v}2}} = \sqrt{\frac{3kT}{m}} \qquad \text{-------- (11)}$$

$$= 1.732\sqrt{\frac{kT}{m}}$$

Thus $v_p < \tilde{v} < v_{rms}$

**Principles of Equipartition of Energy:**

The total energy of a particle of a system in thermodynamic equilibrium can be expressed as the sum of independent squared terms in position and momentum coordinates. For example, the K.E. E of a free particle of mass , m which has velocity v and momentum p can be expressed as

$$E = \frac{{p_x}^2 + {p_y}^2 + {p_z}^2}{2m} \qquad \text{------------ (1)}$$

For a particle of mass m moving with simple harmonic motion along the x-axis, the total energy

$$E = \frac{{p_x}^2}{2m} + \frac{1}{2}Cx^2 \qquad \text{---------------- (2)}$$

where C is the force constant per unit displacement from the mean position. Each independent squared term in the expression for the energy of a particle is said to give rise to one degrees of freedom of the particles. Thus a free particle has three degrees of freedom, and a particle moving with a linear simple harmonic motion has two degrees of freedom.

The principle of equipartition of energy is stated as follows:

When a system in a thermodynamic equilibrium at absolute temperature T, the mean value of each quadratic term in either a position or a momentum coordinate, which occurs in the total energy of the particle is (1/2)kT.

The principle may also be stated as follows:

When a system is in thermodynamic equilibrium at absolute temperature T, the mean energy of a particle in the system is distributed equally among its various degrees of freedom and for each of them it is (1/2)kT.

The principle was first deduced by Maxwell in 1959 for the energy of translational motion of a free particle. Boltzmann later showed that the principle is true for the energies of the rotation and vibration also. Rigorous proof's from statistical mechanics were given later by other workers.

*Proof of the Principles:*

We will prove the principle by finding the mean value of the term $\frac{p_x}{2m}$ in the expression for the energy of a particle in a linear S.H.M. along the X-axis.

The mean value of $\frac{p^2}{2m}$ at equilibrium is given by

$$\langle\frac{p^2}{2m}\rangle = \frac{\int\int\int\int\int\int \frac{p^2}{2m} e^{-\frac{E}{kT}}\, dxdydzdp_xdp_ydp_z}{\int\int\int\int\int\int e^{-\frac{E}{kT}}\, dxdydzdp_xdp_ydp_z}$$

Where E is the total energy.

Writing the exponential term as

$$e^{-\frac{E}{kT}} = e^{-(\frac{{p_x}^2}{2m}+Eo)/kT}$$

$$= e^{-\frac{{p_x}^2}{2mkT}+} \; e^{-Eo/kT}$$

Where $E_0$ is the contribution to the total energy due to all the coordinates and momenta expect $P_x$, we get

$$\langle\frac{{p_x}^2}{2m}\rangle = \frac{\int \frac{{p_x}^2}{2m} e^{-\frac{{p_x}^2}{2mkT}}\; dp_x \int\int\int\int\int e^{-\frac{Eo}{kT}}\, dxdydzdp_ydp_z}{\int e^{-\frac{{p_x}^2}{2mkT}}\; dp_x \int\int\int\int\int e^{-\frac{Eo}{kT}}\, dxdydzdp_ydp_z}$$

Cancelling the five –fold integral in the numerator and denominator, we obtain

$$\langle\frac{{p_x}^2}{2m}\rangle = \frac{1}{2m}\frac{\int_{-\infty}^{\infty} {p_x}^2 e^{-\frac{{p_x}^2}{2mkT}}\; dp_x}{\int_{-\infty}^{\infty} e^{-\frac{{p_x}^2}{2mkT}}\; dp_x} \qquad \text{-------- (3)}$$

Let, $\frac{{p_x}^2}{2mkT} = u^2$

So that $p_x = \sqrt{(2mkT)}\, u$

$dp_x = \sqrt{(2mkT)}\, du$

$$\text{hence, } \langle\frac{{p_x}^2}{2m}\rangle = \frac{1}{2m}\frac{\int_{-\infty}^{\infty} (2mkT)\, u^2 e^{-u^2}\; \sqrt{(2mkT)}\, du}{\int_{-\infty}^{\infty} e^{-u^2}\; \sqrt{(2mkT)}\, du}$$

$$= kT \,.\, \frac{\int_{-\infty}^{\infty} u^2 e^{-u^2}\; du}{\int_{-\infty}^{\infty} e^{-u^2}\; du} \qquad \text{----------- (4)}$$

now evaluate the integral in the numerator.

$$I= \int_{-\infty}^{\infty} u^2 e^{-u^2} \quad du = \int_{-\infty}^{\infty} u.(ue^{-u})^2 \quad du$$

Integrating by parts, we obtain

$$I= u \int u\, e^{-u^2} \quad du - \int \left[\frac{du}{du} . \int u\, e^{-u^2} \quad du\right] du$$

$$= - ½ \left[ue^{-u^2} \quad \right] +1/2 \int_{-\infty}^{\infty} e^{-u^2} \quad du$$

It can be shown that the first term is zero at both the limits. Hence $\int_{-\infty}^{\infty} u^2 e^{-u^2} \quad du$ = ½ $\int_{-\infty}^{\infty} e^{-u^2} \quad du$. Sub this in eq. 4, $\langle \frac{{p_x}^2}{2m} \rangle = \frac{1}{2} kT$ --------- (5)

By a similar proof we can shoe that the mean value (1/2)C $x^2$ is (1/2) kT. Thus the mean energy of one- dimension harmonic oscillator is

$$\langle \frac{{p_x}^2}{2m} \rangle + \langle \frac{1}{2} C\, x^2 \rangle = ½ \text{ kT} + ½ \text{ kT} = \text{kT}$$

In the case of a free particle of the total K E

$$E = \frac{{p_x}^2+{p_y}^2+{p_z}^2}{2m}$$

The mean energy is

$$\langle \frac{{p_x}^2}{2m} \rangle + \langle \frac{{p_y}^2}{2m} \rangle + \langle \frac{{p_z}^2}{2m} \rangle = \frac{1}{2} kT + \frac{1}{2} kT + \frac{1}{2} kT = \frac{3}{2} kT$$

*Limitation of the principle of equipartition of Energy:*

Theoretical values of the specific heat capacities of substances calculated from the equipartition of energy show that they should be independent of the temp. But the experimental result shows that the conclusion is not true. The effect of temperature on the specific heat capacity is considerable. The specific heat capacity increases with increase in temperature, and it decreases when the temperature is lowered. At low temperatures its rate of decrease with decrease of temperature is large both for solids and gases. The effect cannot be explained in any way by classical mechanics and the equipartition principle.

**Partition function Z**

$$N = e^{-\alpha}\Sigma_r g_r e^{-E/kT}$$

$$= A\sum_r g_r e^{-E/kT} \quad \text{--------- (1)}$$

$$\text{Where } A = e^{-\alpha}$$

The summation in eq. (1) is taken over all integrals of r corresponding to all possible energy states of the particles. The summation term is called the partition function or the sum over states and is denoted by the symbol Z. Thus

$$Z = \sum_r g_r e^{-E/kT} \quad \text{------------- (2)}$$

Now in terms of Z, eq. (1) is written as $N = AZ = e^{-\alpha}Z$ ------------ (3)

Using this relation the Maxwell-Boltzmann distribution law $n_r = e^{-\alpha}g_r e^{-E/kT}$

Is written in the form

$$n_r = N/Z \text{ x } g_r e^{-Er/kT} \quad \text{----------- (4)}$$

the multiplier α can be expressed as follows

$$e^{-\alpha} = N/Z$$

$$-\alpha = \log (N/Z) = -\log (Z/N) \quad \text{----------------- (5a)}$$

$$\alpha = -\log (N/Z) = \log (Z/N) \quad \text{------------------ (5b)}$$

*Evaluation of Z*

$$Z = N/A = \frac{N}{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}}$$

$$= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \quad \text{------------ (6)}$$

This equation gives the value of the partition function for an ideal gas consisting of mono atomic having no spin

**Condition for applicability of the Maxwell-Boltzmann statistics**

The M-B statistics is applicable to a system of identical particles which do not interact with each other directly except during their collisions. The condition whether neutral particles in a system will interact with each other or not determined by calculating their de Broglie wavelength.

If the wavelength is smaller than the mean distance between the particles, then the particles will not interact. Thus if $\lambda$ is the de Broglie wavelength and d the mean distance between the particles, the condition for application of M-B statistics is $\lambda < d$ ------- (1)

To express this condition in terms of the degeneracy parameter $e^{-\alpha}$ the expression for d and $\lambda$.

The volume per particle = V/N

Therefore the mean distance d between the particles is

$$d=(V/N)^{1/3} \qquad \text{-------- (2)}$$

The mean K.E. of the particles is (3/2) kT. Therefore, the corresponding momentum p is given by

$$\frac{p^2}{2m} = \frac{3}{2}kT$$

$$p = \sqrt{(3mkT)}$$

$$\text{and } \lambda = h/p = h / \sqrt{(3mkT)}$$

$$= \left(\frac{h^2}{3mkT}\right)^{1/2} \qquad \text{-------- (3)}$$

Sub. the values of d and $\lambda$ in condition (1),

$$\left(\frac{h^2}{3mkT}\right)^{1/2} < \left(\frac{V}{N}\right)^{1/3}$$

$$\text{Or} \quad \left(\frac{h^2}{3mkT}\right)^{3/2} < (V/N)$$

$$\text{Or } \left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} (N/V) < 1$$

Multiplying by $(3/2\pi)^{3/2}$,

$$(3/2\pi)^{3/2} \text{ x } \left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} \left(\frac{N}{V}\right) < (3/2\pi)^{3/2}$$

$$\left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} \left(\frac{N}{V}\right) < 0.33$$

$$\text{Or} \qquad e^{-\alpha} << 1$$

$$\text{Or} \qquad A<<1$$

**Non –degenerate and degenerate systems**

If the number of particles, $n_r$ in an energy level $E_r$ is much less than the number of quantum states, $g_r$ available in the same energy level i.e,, if $n_r << g_r$ the system of particles is said to be non degenerate.

If $n_r$ is greater than $g_r$ i.e, if $n_r > g_r$ the system is said to be degenerate.

If $n_r$ is much greater than $g_r$,i.e,, if $n_r >> g_r$ the system is said to be strongly degenerate.

The degeneracy parameter A($e^{-\alpha}$) is given by

$$A = e^{-\alpha} = \frac{n_r}{g_r{}^{e^{-\beta E}}}$$

If we consider the ground state as a zero, then

$$A = e^{-\alpha} = \frac{n_0}{g_0}$$

Therefore in terms of A is foregoing conditions are as follows:

1. If A<<1, the system is non-degenerate.

2. If A>1, the system is degenerate.

3. If A >>1, the system is strongly degenerate.

**Maxwell velocity distribution in a given direction**

In a system of an ideal gas the number of molecules having velocity components in the range between $v_x$and $v_x+dv_x$, $v_y$ and $v_y+dv_y$ and $v_z$ and $v_z+dv_z$ is given by

$$n\,(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = [f\,(v_x, v_y, v_z)]\, [g(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z] \qquad \text{------- (1)}$$

The first term on the R.H.S of this equation is the distributed function for the velocity components, i.e., it is the number of molecules each having the velocity components $v_x$ $v_y$ $v_z$ per quantum state in the energy level E. The second term is the number of quantum states within the velocity space $dv_x$ $dv_y$ $dv_z$. These terms are obtained as follows.

$$f\,(E) = \frac{N}{V}\,\left(\frac{h^2}{2\pi mKT}\right)^{3/2} e^{-E/kT} \qquad \text{------- (2)}$$

Assuming that each molecule has only three degrees of freedom due to its motion of translation, the K.E of each molecule is given by

$$E = ½\, mv^2$$

$$= ½\, m\,(v_x^2 + v_y^2 + v_z^2) \qquad \text{------- (3)}$$

From eq. (2), $f\,(v_x, v_y, v_z) = \frac{N}{V}\,\left(\frac{h^2}{2\pi mKT}\right)^{3/2} e^{-m(v_x{}^2 + v_y{}^2 + v_z{}^2)/kT}$ ----------- (4)

The volume of one quantum state in the momentum space is $h^3/V$, where V is the physical volume of the system.

Therefore the number of quantum states in volume $dp_x$ $dp_y$ $dp_z$ of momentum space.

$$= V/h^3\, dp_x\, dp_y\, dp_z$$

$$= m^3V/h^3\, dv_x\, dv_y\, dv_z$$

Hence $g\,(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = m^3V/h^3\, dv_x\, dv_y\, dv_z$ --------- (5)

Sub. Eq. (4) and (5) into (1)

$$n\,(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = \frac{N}{V}\,\left(\frac{h^2}{2\pi mKT}\right)^{3/2} m^3V/h^3\, e^{-m(v_x{}^2 + v_y{}^2 + v_z{}^2)/kT}\, dv_x\, dv_y\, dv_z$$

Simplifying this equation,

$$n\ (v_x, v_y, v_z)\ dv_x\ dv_y\ dv_z = N\ (\frac{m}{2\pi KT})^{3/2}\ x\ e^{-\ m\ (v_x{}^2 + v_y{}^2 + v_z{}^2)/kT}\ dv_x\ dv_y\ dv_z \qquad \text{-------- (6)}$$

Now the number $n\ (v_x)\ dv_x$ of molecules, having x component of velocity in the range between $v_x$ and $v_x+dv_x$ is obtained by integrating eq. (6) over all possible values of $v_y$ and $v_z$.

$$n\ (v_x)\ dv_x = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}[n\ (\ v_x, v_y, v_z)dv_x]\ dv_y\ dv_z$$

$$= N\ (\frac{m}{2\pi KT})^{3/2}\ e^{-mv_x{}^2/2kT}\int_{-\infty}^{\infty} e^{-mvy2/2kT}\ \int_{-\infty}^{\infty} e^{-mvy2/2kT}$$

The definite integrals are standard integrals, the value of each being

$$[(2\pi kT)/m]^{1/2}$$

Sub. this value in above equation ,

$$n\ (v_x)\ dv_x = N\ (\frac{m}{2\pi KT})^{3/2}(\frac{2\pi KT}{m})\ e^{-mv_x{}^2/2kT}\ dv_x$$

$$= N\ (\frac{m}{2\pi KT})^{1/2}\ e^{-mv_x{}^2/2kT}\ dv_x \qquad \text{---------- (7)}$$

This equation gives the number of molecules having x component of velocity in the range between $v_x$ and $v_x+dv_x$. Eq. (7) shows that the velocity component $v_x$ is distributed symmetrically about the value $v_x = 0$.

**Total internal energy of an ideal gas**

The total internal energy of an ideal gas is given by

$$U = \int_0^{\infty} E\ n(E)dE \qquad \text{-------- (1)}$$

$$= \int_0^{\infty} E\ \left[\frac{2\pi N}{(\pi kT)^{3/2}}\ E^{\frac{1}{2}}e^{-\frac{E}{kT}}dE\right]$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}}\ \int_0^{\infty}\ \left[E^{\frac{3}{2}}e^{-\frac{E}{kT}}dE\right] \qquad \text{----------- (2)}$$

Let E/kT = x, so that E = kTx

Therefore dE = kTdx

Sub. These values in eq. (2) get

$$=\frac{2\pi N}{(\pi kT)^{3/2}}(kT)^{3/2}kT\int_0^\infty x^{3/2}\, e^{-x}\, dx$$

$$=\frac{2NkT}{\sqrt{\pi}}\int_0^\infty x^{\frac{5}{2}-1}\, e^{-x} dx \qquad \text{------- (3)}$$

The integral is the gamma function

$$\Gamma(5/2) = 3/2\ \Gamma(3/2) = 3/2 \times ½ \times \sqrt{\pi} = 3\sqrt{\pi} / 4$$

Sub. This value in eq. (3) ,

$$U = \frac{2NkT}{\sqrt{\pi}} \times \frac{3\sqrt{\pi}}{4} = \frac{3}{2}NkT \qquad \text{----------- (4)}$$

From this equation, the average internal energy per molecule is given by $U / N = \frac{3}{2}kT$ ------ (5)

For 1 mole of an ideal gas, N is Avagadro's number and the value of U is given by eq. (4) is the total internal energy of one mole of an ideal gas.

**Molar Heat Capacity of a gas at Constant Volume**

The molar heat capacity $C_v$, of a gas at constant volume is defined as the quantity of heat required to raise the temperature of 1 mole of the gas through 1 degree, at constant volume.

According to the definition

$$C_v=\left(\frac{\partial U}{\partial T}\right)_V$$

$$=\frac{\partial}{\partial T}\left(\frac{3}{2}NKT\right)=\frac{3}{2}NK \qquad \text{-------------------(1)}$$

$$C_v=\frac{3}{2}\, N\left(\frac{N}{R}\right)= \frac{3}{2}R \qquad \text{--------------------(2)}$$

Where R is the gas constant for one mole.

**Entropy**

According to Boltzmann's relation, the entropy S of an isolated system of non-interacting particles in equilibrium is given by

$$S = k \log W_{max} \qquad \text{------- (1)}$$

Where $W_{max}$ is the maximum number of statistically independent ways of distributing the particles among the quantum states. From the M-B count,

$$\log W = N \log N - N + \Sigma_r n_r (\log g_r - \log n_r + 1)$$

$$= N \log N - N + \Sigma_r n_r \log (g_r/n_r) + N$$

$$= N \log N - \Sigma_r n_r \log (n_r/g_r)$$

For maximum value of W

$$n_r/g_r = e^{-(\alpha+\beta E_i)}$$

Therefore, $\log W_{max} = N \log N + \Sigma_r n_r (\alpha+\beta E_r)$

$$= N \log N + \alpha \Sigma_r n_r + \beta \Sigma_r n_r E_r$$

$$= N \log N + \alpha N + \beta U \qquad \text{----------- (2)}$$

Where U is the total internal energy

Sub. $\beta = 1/kT$ and $\alpha = \log (Z/N)$

Where Z is the partition function,

$$\log W_{max} = N \log N + N \log \frac{Z}{N} + \frac{U}{kT}$$

$$= \frac{U}{kT} + N \log Z \qquad \text{---------- (3)}$$

Sub. this value of $\log W_{max}$ in eq. (1),

$$S = U/T + Nk \log Z \qquad \text{----------(4)}$$

For an ideal gas, $U = \frac{3}{2}$ NkT and $Z = V\left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}}$

According to M-B count, the entropy of an ideal gas is

$$S = \frac{3}{2}\text{Nk} + \text{Nk}\log\left[V\left(\left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}}\right)\right] \qquad \text{-------- (5)}$$

**Helmholtz Free Energy**

The Helmholtz Free Energy F of a system of particles is defined by

$$F=U-TS \qquad \text{----------------(1)}$$

The entropy of a system is given by

$$S=\frac{U}{T}+NK+NK\log\frac{Z}{N}$$

Subs this value in eq (1)

$$F=U-T[\frac{U}{T}+NK+NK\log\frac{Z}{N}]$$

$$=-NKT(log\frac{Z}{N}+1) \qquad \text{----------(2)}$$

$$=-NKT[\log Z-\log N+1] \qquad \text{----------- (3)}$$

Eq(3) can be expressed in

$$F=-NKT\log Z + NKT\log N - NKT$$

$$=-NKT\log Z+KT(N\log N-N)$$

$$=-NKT\log Z+KT\log N!$$

**Pressure and Equation of State of an Ideal gas**

The Helmholtz free energy F is

$$F=U-TS$$

Taking differential

$$dF=dU-TdS-SdT \qquad \text{--------------------(1)}$$

from the first and second law of thermodynamics for a reversible process we get

$$dU=TdS-PdV$$

$$\text{or } dU-TdS=-pdV \qquad \text{-----------------(2)}$$

Therefore eq (1)

$$dF=-pdV-SdT \qquad \text{-----------------(3)}$$

This equation shows that F is a function of the independent variable V and T

$$F=f(V,T)$$

Therefore

$$dF=\left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial V}\right)_V dT \qquad \text{--------------------(4)}$$

Equating the co efficient of dV in eq(3) and (4) we get

$$P=-\left(\frac{\partial F}{\partial V}\right)_T \qquad \text{------------------------(5)}$$

An expression for F is

$$F=-NKT\,[\log Z - \log N + 1]$$

From eq(5) we get

$$P=NKT\left(\frac{\partial \log Z}{\partial V}\right)_T \qquad \text{----------------------(6)}$$

For an ideal monatomic gas the partition function z is given by

$$Z=V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

By taking log to base e

$$\log Z = \log V + \frac{3}{2}\log\left(\frac{2\pi mKT}{h^2}\right)$$

By diff. partially we get

$$\frac{\partial \log Z}{\partial V}=\frac{1}{V}$$

subs this value in eq(6)

$$P=\frac{NKT}{V} \qquad \text{----------------------(7)}$$

In this equation K is Boltzmann's constant ($1.38\text{x}10^{-23}$J/K),and for 1 mole of a gas N is Avogardro's number($6.023\ \text{x}10^{23}$/mol).Therefore, for one mole the product NK is the same for all gases. This constant is called molar gas constant denoted by the symbol R. So for 1 mole of a gas eq(7) in the form

$$PV=RT \qquad \text{---------------------(8)}$$

This equation for one mole of an ideal gas is called the equation of state for the gas. The numerical value of R is

$$R=Nk=(6.023\ \text{X}10^{23}/\text{mol})(1.38\ \text{x}10^{-23}\ \text{J/K})$$

$$=8.31\ \text{J/mol K}$$

**Limitations of Maxwell-Boltzmann Method**

The method has several limitations, some of them are

1. It is applicable to only isolated gas of identical molecules in equilibrium, for which the following conditions are satisfied.
   i. The mean potential energy due to interaction b/w the molecules are very small compared to their mean K E.
   ii. The gas is dilute i.e, the number of molecules per unit volume is small, so the average separation between the molecules is large and hence individual molecules can be distinguished.

Therefore, important results, such as the expression for u, $c_v$ and p, obtained by this method are the same as those delivered by applying a simple kinetic theory.

2. The expression for the Maxwell-Boltzmann count does not give the correct expression for the entropy of an ideal gas, and leads to Gibbs'paradox. To resolve the Paradox the expression must be divided by N!.
3. In the expression for the entropy of an ideal gas

$$S=NK\log[(\frac{2\pi mKT}{h^2})e^{5/2}]$$

if we put T=0, we get

$$S=NK\log 0=-\infty.$$

Thus the expression for S does not satisfy the third law of thermodynamics which may be started as follows: Every substance has a finite positive entropy, but an absolute zero of temperature the entropy may become zero, and it becomes zero in case of perfectly crystalline solid.

4. It cannot be applied to a system of indistinguishable particle. If we apply the Maxwell – Boltzmann distribution law of thermionic emission, we get the following expression for the emission current density

$$J=A_0T^{1/2}e^{-\frac{\Phi}{KT}}$$

which is not correct .The correct Expression which has been verified as

$$J=A_cT^2e^{-\frac{\Phi}{KT}}$$

## Possible Questions

1. What is meant by partition function?
2. What are called boson?
3. Define molar heat capacity of a gas.
4. Define degenerate and non-degenerate system.
5. Explain the principle of equipartition of energy.
6. Derive an expression for pressure and the equation of state of an ideal gas.
7. What are the limitations of M-B statistics?
8. Obtain Helmhotz free energy.
9. Obtain an expression for most probable, average and root mean square speeds.
10. Explain the limitations of M.B. method.
11. Calculate total internal energy of an ideal gas.
12. Evaluate constant value of M.B. statistics.
13. Explain M.B. distribution law.
14. What are the conditions for applicability of M.B. statistics?

Enable | Enlighten | Enrich
KARPAGAM
ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956 )

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**

**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT III (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | Which is called as degeneracy parameter? | $e^{\alpha}$ | $e^{\beta}$ | $ce^{-\alpha}$ | $e^{+\beta}$ | $e^{-\alpha}$ |
| 2 | Partition function is denoted by the symbol____ | Z | A | M | N | Z |
| 3 | Mean distance d between the particles is _____ | $(N/V)^{1/3}$ | $(V/N)^{1/3}$ | $(N/V)^{3}$ | $(V/N)^{3}$ | $(V/N)^{1/3}$ |
| 4 | If A<<1, the system is _________ | non- degenerate | degenerate | strongly degenerate | weekly degenerate | non- degenerate |
| 5 | If A>1, the system is _________ | non- degenerate | degenerate | strongly degenerate | weekly degenerate | degenerate |
| 6 | If A>>1, the system is _______ | non- degenerate | degenerate | strongly degenerate | weekly degenerate | strongly degenerate |
| 7 | The number of quantum states is represented by _____ | $n_r$ | $g_r$ | $E_r$ | N | $g_r$ |
| 8 | The degeneracy parameter A = _________ | Z | $e^{\alpha}$ | $e^{-\alpha}$ | $e^{\beta}$ | $e^{-\alpha}$ |
| 9 | In M.B. distribution, the unit of n(v) is ______ | m/ sec | mol/sec | mol/m/sec | sec | mol/m/sec |
| 10 | $v_p =$ ___ | $\sqrt{(2kT/m)}$ | $1.414\sqrt{kT}$ | $1.732\sqrt{(kT/m)}$ | $3.414\sqrt{kT}$ | $\sqrt{(2kT/m)}$ |
| 11 | Average speed is represented by ___ | $v_p$ | v | Av | $v_{rms}$ | $v_p$ |
| 12 | Which of the following is correct for a perfect gas? | $v<v_p<v_{rms}$ | $v_p<v<v_{rms}$ | $v<v_{rms}<v_p$ | $v>v_p>v_{rms}$ | $v_p<v<v_{rms}$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| 13 | Root mean square = ________ | √ (2kT/m) | 1.414√ kT | 1.732√(kT/m) | 3.414√kT | 1.732√(kT/m) |
| 14 | Average speed = _________ | 1.596√(kT/m) | 1.414√ kT | 1.732√(kT/m) | 3.414√kT | 1.596√(kT/m) |
| 15 | The equation for total internal energy of one mole of an ideal gas is _______ | U/N = 3/2 kT | U/N = 3/2 | U/N = kT | U/N = 2/3 kT | U/N = 3/2 kT |
| 16 | The value of β = ______ | kT | k | T | 1/kT | 1/kT |
| 17 | At absolute zero temperature the entropy may become __________ | Infinity | positive | Zero | Negative | Zero |
| 18 | The value of entropy becomes zero in perfectly _______ | liquid | crystalline solid | gas | inert gas | crystalline solid |
| 19 | M.B. law cannot be applicable to ______ particles. | distinguishable | Indistinguishable | isolated | Isobaric | Indistinguishable |
| 20 | In dilute gas, the number of molecules per unit volume is _____ | large | very small | infinity | small | small |
| 21 | In dilute gas, the average separation between the molecules is ______ | large | very small | Infinity | small | large |
| 22 | The mean energy of principle of equipartition of energy is ______ | kT | 3/2 kT | 2/3 kT | ½ kT | 3/2 kT |
| 23 | A free particle has ___________ degrees of freedom. | 1 | 2 | 3 | 4 | 3 |
| 24 | A particle moving with a linear simple harmonic motion has ___ degrees of freedom. | 1 | 2 | 3 | 4 | 2 |
| 25 | Helmhotz free energy F of a system of particles is defined by _______. | F=U-TS | F=U/TS | F=U+TS | F=UTS | F=U-TS |
| 26 | The specific heat at constant volume is | the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant pressure | the amount of heat required to raise the temperature of 1 kg of water through one degree | the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume | any one of the above | the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume |
| 27 | The gas constant (R) is equal to the __________ of | sum | difference | product | ratio | difference |

| | | | | | | |
|---|---|---|---|---|---|---|
| | two specific heats. | | | | | |
| 28 | The quantum statistics reduces to classical statistics under the following condition | $\rho\lambda^3 = 1$ | $\rho\lambda^3 >> 1$ | $\rho\lambda^3 << 1$ | $\rho\lambda^3 = 0$ | $\rho\lambda^3 >> 1$ |
| 29 | Specific heat of metals can be expressed as ___ | $T^3$ | $AT + BT^2$ | $AT^2+BT^3$ | $AT + BT^3$ | $AT + BT^3$ |
| 30 | Boltzmann entropy probability relation is given by _______ | $S=k \log_e\omega$ | $S = k/\log_e\omega$ | $S = k+\log_e\omega$ | $S = k-\log_e\omega$ | $S=k \log_e\omega$ |
| 31 | Enthalpy and internal energy have relation ______ | H= U –PV | H= U/PV | H=U+PV | H=UPV | H=U+PV |
| 32 | In quantum physics identical particles are ______ | a) indistinguishable | distinguishable | symmetric | anti-symmetric | indistinguishable |
| 33 | The zero point energy of one dimensional oscillator is _____ | 2h | ½ h | 1/3 h | 3h | ½ h |
| 34 | In classical physics identical particles are ______ | indistinguishable | distinguishable | symmetric | anti-symmetric | distinguishable |
| 35 | The dimensions of the phase space depends upon the ____ of the system. | entropy | heat content | degrees of freedom | enthalpy | degrees of freedom |
| 36 | _________of a system of particles is given by $F = U - TS$ | Helmholtz free energy | free energy | helmholtz function | Gibb's free energy | Helmholtz free energy |
| 37 | For non-degenerate system | A= 1 | A<< 1 | A> 1 | A>= 1 | A<< 1 |
| 38 | The spin of the photon is | 0 | 1 | 2 | ½ | 1 |
| 39 | B.E distribution function is given by | $\{1/( e^{a + bE}) \}$ | $\{1/( e^{a + bE}) + 1\}$ | $\{( e^{a + bE}) - 1\}$ | {1/( ea + bE) – 1} | $\{( e^{a + bE}) - 1\}$ |
| 40 | The degeneracy parameter $e^{-a}$ = | $N/V ( h^2 / 2pmkT )^{1/2}$ | $N/V ( h^2 / 2pmkT )^{3/4}$ | $N/V ( h^2 / 2pmkT )^{3/2}$ | $N/V ( h^2 / 2pmkT)^3$ | $N/V ( h^2 / 2pmkT )^{3/2}$ |
| 41 | Maxwell first developed ____________theory | Equipartition | partition | classical | quantum | classical |
| 42 | According to classical mechanics a molecule can have | finite speed | infinite speed | variable speed | constant speed | infinite speed |
| 43 | As temperature increases, the most probable __________also increases | frequency | wavelength | energy | velocity | velocity |
| 44 | B.E distribution law is used to derive ___________of radiation | Plank's law | Weiss law | Widemann-Franz law | All the above | Plank's law |
| 45 | Wave function of the system of identical Bosons is | Asymmetric | linear | non-linear | symmetric | symmetric |
| 46 | M.B. distribution can be applicable to _________ | identical | indistinguishable | gas | liquid | identical |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | molecule | molecule |  |  | molecule |
| 47 | In M.B. distribution the mean P.E. is ______ than/ to K.E. of ideal gas. | larger | very large | small | equal | small |
| 48 | When T=0, the value of entropy S = ______ in M.B. distribution. | infinity | negative infinity | zero | one | negative infinity |
| 49 | The correct expression for J = __________ | $A_C T^2 e^{-\varphi/kT}$ | $A_C T e^{-\varphi/kT}$ | $A_C T^{1/2} e^{-\varphi/kT}$ | $T^2 e^{-\varphi/kT}$ | $A_C T^2 e^{-\varphi/kT}$ |
| 50 | The value of gas constant R= _____ | 8.13K/mol | 7.013 mol/K | 8.31 mol/JK | 8.31 J/mol K | 8.31 J/mol K |
| 51 | Partition function is denoted by the symbol____ | Z | A | M | N | Z |
| 52 | Mean distance d between the particles is _____ | $(N/V)^{1/3}$ | $(V/N)^{1/3}$ | $(N/V)^3$ | $(V/N)^3$ | $(V/N)^{1/3}$ |
| 53 | In M.B. distribution, the unit of n(v) is ______ | m/ sec | mol/sec | mol/m/sec | sec | mol/m/sec |
| 54 | $v_p$ = ___ | $\sqrt{(2kT/m)}$ | $1.414\sqrt{kT}$ | $1.732\sqrt{(kT/m)}$ | $3.414\sqrt{kT}$ | $\sqrt{(2kT/m)}$ |
| 55 | Root mean square = ________ | $\sqrt{(2kT/m)}$ | $1.414\sqrt{kT}$ | $1.732\sqrt{(kT/m)}$ | $3.414\sqrt{kT}$ | $1.732\sqrt{(kT/m)}$ |
| 56 | The equation for total internal energy of one mole of an ideal gas is _______ | U/N = 3/2 kT | U/N = 3/2 | U/N = kT | U/N = 2/3 kT | U/N = 3/2 kT |
| 57 | M.B. law cannot be applicable to ______ particles. | distinguishable | Indistinguishable | isolated | Isobaric | Indistinguishable |
| 58 | The mean energy of principle of equipartition of energy is ______ | kT | 3/2 kT | 2/3 kT | ½ kT | 3/2 kT |

## UNIT-IV

**Quantum Statistical Mechanics:** B.E energy distribution for energies in the range E to E + dE – Condition for B.E distribution to approach classical M.B distribution - Bose temperature - Bose Einstein condensation - Planck’s law from B.E law - Fermi Dirac distribution law (no derivation) - FD law for the energies in the range E to E+dE – Fermi energy - Effect of temperature - Energy distribution curve - Free electron in a metal - Fermi temperature and Thermionic emission - Richardson Dushmann Equation - Comparison of MB,BE and FD statistics.

**Bose Einstein energy distribution for energies in the range E to E + dE**

The molecules of an ordinary gas have spin angular momentum equal to an integral multiple of ħ. It means that the molecules are bosons and they will obey the Bose-Einstein statistics. The energy distribution law for a system of identical molecules is obtained as follows.

The number n (E) dE of the molecules having energies in the range from E to E+dE is given by

$$n(E)\, dE = f(E)\, g(E)\, dE \qquad \text{---------------} \ (1)$$

where f(E) is the energy distribution function, and g (E)dE is the number of quantum states available in the energy range.

Substituting the expression for f (E) in equation (1), obtained

$$n\,(E)dE = \frac{g\,(E)dE}{e^{\alpha}e^{E/kT} - 1} \qquad \text{-----------} \ (2)$$

$$g\,(E)\,dE \text{ is given by, } g\,(E)\,dE = 2\pi V\,\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\, dE$$

Substituting this equ. in (2)

$$n(E)\, dE = 2\pi V\,\left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{E^{\frac{1}{2}}dE}{e^{\alpha}e^{E/kT} - 1} \qquad \text{-------} \ (3)$$

This is Bose Einstein energy distribution law given by the number of particles with energies between E and E +dE.

The constant $e^{\alpha}$ appears in the distribution law cannot be less than or equal to 1 because

(i) if $e^{\alpha}$ is <1, then for E = 0

$$n\,(E)dE = \frac{g\,(E)dE}{e^{\alpha}e^{E/kT} - 1}$$

$n\,(0)dE = \frac{g\,(0)dE}{e^{\alpha} - 1}$ = negative quantity

$$\textit{which is impossible.}$$

(ii) if $e^{\alpha}$ = 1, then for E = 0

$n\,(0)dE = \frac{g\,(0)dE}{1 - 1} = \infty$

Which is also impossible. Therefore $e^{\alpha}$ must be greater than 1.

**Condition for B-E distribution to approach classical M-B distribution:**

The B-E distribution is given by

$$n(E)\, dE = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{E^{\frac{1}{2}} dE}{\frac{1}{A}\, e^{E/kT} - 1} \quad \text{----------- (1)}$$

If 1 in the denominator is neglected in comparison with the first term, this distribution will approach the M-B distribution:

$$n(E)\, dE = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} A E^{1/2} e^{-E/kT}\, dE$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{N}{V} \left(\frac{h^2}{2\pi m kT}\right)^{3/2} E^{1/2}\, e^{-E/kT}\, dE$$

$$= \frac{2\pi N}{(\pi kT)3/2} E^{1/2}\, e^{-E/kT}\, dE$$

The condition for this is that

$$\frac{1}{A}\, e^{E/kT} >> 1$$

$$\text{i.e. } \frac{A}{\mathrm{eE/kT}}\, e^{E/kT} << 1$$

For all values of the energy, $e^{E/kT}$ is greater than or equal to 1. Therefore the condition is

$$A << 1.$$

**Limiting Case of Bose-Einstein Statistics**

For an ideal Bose-Einstein distribution the degeneracy parameter A(=$e^{\alpha}$)cannot be greater than 1;its maximum value can be 1.If the temperature of the gas is decreased, the value of A increases from a low value towards 1.At a certain temperature $T_B$, the value of A becomes just less than 1,and then there is no change in the value below $T_B$ .At $T_B$ some proportion of the molecules start reaching the zero-energy state. This critical temperature is called the Bose temperature.

*Expression for the Bose Temperature:*

In the ideal Bose-Einstein gas of spin less molecules in the thermal equilibrium at the temperature T, the tot al number of N molecules is given by

$$N= 2\pi V(\frac{2mkT}{h^2})^{3/2}\int_0^2 \frac{x^{1/2}}{e^{\alpha}e^{x}-1}\,dx$$

Where

$$x=E/kT$$

The value of integral

$$N= 2\pi V(\frac{2mkT}{h^2})^{3/2}\frac{\sqrt{\pi}}{2}\left[\frac{1}{e^{\alpha}}+\frac{1}{2^{\frac{3}{2}}e^{2\alpha}}+\frac{1}{3^{\frac{3}{2}}e^{3\alpha}}+\ \ldots\ldots\right]$$

Substituting the value $e^{1/A} = e^{-\alpha} = A$

$$N= V(\frac{2\pi mkT}{h^2})^{3/2}\left[\frac{A}{1}+\frac{A^2}{2^{\frac{3}{2}}}+\frac{A^3}{3^{\frac{3}{2}}}+\ \ldots\ldots\right]$$

At Bose Temperature $T=T_B$,

$$N=V(\frac{2\pi mkTB}{h^2})^{3/2}\left[1+\frac{1}{2^{\frac{3}{2}}}+\frac{1}{3^{\frac{3}{2}}}+\ \ldots\ldots\right]$$

The series in the square bracket is the Riemann Zeta function whose value is 2.612.

$$N=V\,(\frac{2\pi mkTB}{h^2})^{3/2}\ \text{x}\ 2.612$$

$$=2.612\ V(\frac{2\pi mkTB}{h^2})^{3/2} \qquad \text{--------(1)}$$

Where

$$T_B=\left(\frac{h^2}{2\pi mk}\right)\ (N / 2.612\ V)^{3/2} \qquad \text{---------(2)}$$

For all known Bose-Einstein gas, the Bose temperature $T_B$ is very low. For ex, for helium $({}_2He^4)T_B= 3.15$ K

*Bose-Einstein condensation:*

At the Bose temperature molecules $T_B$, molecules just start reaching the zero-energy state (E=0) from the higher energy state (E>0). If the temperature of the gas is lowered below $T_B$, the number of molecules in the zero-energy state will increase, and the number in the higher energy states will decrease. Suppose that in thermal equilibrium at the temperature $T< T_B$, $n_0$ is the number of molecules in the non zero- energy state and $N_e$ is the number in the higher energy states. Then

$$N_e=N- n_0 \qquad \text{-------------------- (3)}$$

The zero –energy state occupation number is given by

$$n_0=\frac{g0}{\frac{1}{A}-1} \qquad \text{-------------------- (4)}$$

where $g_0$ is the number of allowed states at energy E=0

$$N_e \text{ is given by,} N_e=2.612V\left(\frac{2\pi mKT}{h2}\right)^{3/2} \qquad \text{-------------------- (5)}$$

and N is given by $N=2.612V\left(\frac{2\pi mKT}{h2}\right)^{3/2}$

div. eq. (5) by eq. (1)

$$\frac{Ne}{N}=\left(\frac{T}{TB}\right)^{3/2}$$

Or $$N_e = N\ (T/T_B)^{3/2} \qquad \text{--------------- (6)}$$

where $T<T_B$

From eq.(3) & eq.(6) $n_0=N-N_e$

$$=N[1-(\frac{T}{TB})^{3/2}] \qquad \text{--------------------} \ (7)$$

This eq. shows that as T approaches absolute zero of temperature $N_e \rightarrow 0$ and $n_0 \rightarrow N$

Thus all the molecules of B-E gas tend to condense into the zero energy states of the gas at absolute zero this phenomenon is called Bose- Einstein condensation. The temperature at which $n_0= N_e=N/2$ obtained by sub. $N_{e=}$ N/2 in eq. (6).

$$\frac{N}{2}=N(\frac{T}{TB})^{3/2}$$

$$T=(\frac{1}{2})^{2/3} T_B$$

$$=0.63 \ T_B$$

The molecules of an ideal B-E gas exist in two phases at $T<T_B$

i. a gaseous phase consisting of $N_e$ molecules distributed among the energy states higher than the ground state, and
ii. a condensed phase consisting of $n_0$ molecules occupying the ground state.

The molecules in the condensed phase do not contribute to the internal energy, specific heat capacity, entropy, etc.

The transition of the molecules at $T_B$ to the ground state is a sudden of phenomenon. In this phenomenon there is a decrease in volume of the momentum space by the volume of the space which $n_0$ molecules had occupied before their transition to the zero-energy state. This differs from the usual type of vapor condensation process in which there is a decrease in the physical volume.

The transition of liquid $_2He^4$-I to superfluid liquid $_2He^4$-II at the observed temperature 2.18K can be expanded by Bose- Einstein condensation process.

**Planck's law of radiation from Bose-Einstein distribution law**

According to planck's radiation law the energy of radiation of wavelength in the range between λ and λ+dλ emitted per unit volume by a perfectly black body at absolute temperature T is given by U (λ)d λ = $\frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{\frac{hc}{kT}}-1}$

*Derivation of law*

According to the Bose- Einstein distribution law the number of Bosons having energies between E and E+dE is

$$n\,(E)dE = \frac{g(E)dE}{e^{\alpha}e^{\frac{E}{kT}}-1} \quad \text{--------} \; (1)$$

where g(E) dE is the number of quantum stage of energies E and E +dE.

Let T be the absolute temperature of a black body chamber of volume v. The chamber is supposed to be filled with photons each having energy h$\nu$ .They move in all possible directions with the speed of light C. Each photon has unit spin angular momentum equal to h(h/2π).Hence photons are bosons and use B.E distribution law to derive Planck's law of radiation.

1. *Constant α*:

Photons of different energies are absorbed and re-emitted by the walls of the chamber at constant temp.

In this process a higher energy photon is converted into a number of low energy photons and vice-versa. Though the total energy of the photons remain constant, the total no of photons present in enclosure is not constant. Therefore the condition $\sum_r n_r$ = N or $\sum_r dn_r$ = 0 is not applicable for the distribution and hence the multiplier α is zero, i.e $e^{-\alpha}$ is equal to 1.

2. *Expression for g(E)dE:*

The number of quantum states corresponding to the momenta in the range between p and p+dp for particles with no spin is given by

$$g(p)\ dp = \frac{4\pi V p^2 dp}{h^3}$$

each photon has unit spin angular momentum, there are two allowed quantum states for each photon. Hence photons of the same energy can have the two different directions of polarization circularly clockwise and circularly anti-clockwise. Taking the spin in to account for photons we have

$$g(p)\,dp = \frac{2\ x\ 4\pi V p^2 dp}{h^3}$$

$$= \frac{8\pi V p^2 dp}{h^3} \qquad \text{---------}\ (2)$$

For photons of frequency ν.

Energy, $E = mc^2 = h\nu$ and momentum $p = mc = mc^2/2 = h\nu/c$

By sub these values in equ. (2), $g(\nu)\,d\nu = \frac{8\pi V \nu^2 d\nu}{c^3}$ -------- (3)

Sub. the values of α and g(E) dE in eq. (1 )

$$n(\nu)\,d\nu = n\,(E)dE$$

$$= \frac{8\pi V}{c^3}\ \nu^2 d\nu/e^{h\nu/kT} - 1 \qquad \text{--------}\ (4)$$

This equ. Gives the number of photons of frequencies between ν and ν + dν in the enclosure of volume v at temp T.

Now the energy per unit volume of the enclosure,of the photons of frequencies between ν and ν + dν is

$$U(\nu)d\,\nu = \frac{h\nu n(\nu)d\nu}{\nu}$$

$$== \frac{8\pi h}{c^3}\nu^3\ d\nu/e^{h\nu/kT} - 1 \qquad \text{------------------}(5)$$

This is this the plancks law of radiation in terms of frequency ν

*Eq*n(5) can be transformed in terms of the wavelength λ by using the relations

$$\nu = \frac{c}{\lambda},\ d\nu = -\frac{c}{\lambda^2}d\lambda$$

The energy u(ν)d ν contained in a frequency interval between ν and ν + dν is equal to the contained in a corresponding wavelength interval b/n λ and λ+ d λ.

$$U(\lambda)d\,\lambda = u(\nu)d\nu$$

$$= \frac{8\pi h}{c^3}\,\frac{\left(\frac{c}{\lambda}\right)3\left(-\frac{c}{\lambda^2}d\lambda\right)}{ eh\nu/kT - 1}$$

Omitting the negative sign we get,

$U(\lambda)d\,\lambda = \frac{8\pi hc}{\lambda^5}\, d\lambda \,/\, e^{h\nu/kT} - 1$ ------------------------------- (6)

This is the planck's law of radiation in terms of wavelength λ

**Fermi –Dirac distribution law**

In F-D statistics, the condition are:

(i) The particles are indistinguishable from each other i.e., there is no restriction between different ways in which $n_i$ particles are chosen.

(ii) Each sublevel or cell may contain 0 or one particle. Obviously $g_i$ must be greater than or equal to $n_i$.

(iii) The sum of energies of all particles in the different quantum groups taken constitutes the total energy of the system.

The Fermi – Dirac statistics is given by

$$n_i = \frac{g_i}{e^{(\alpha+\beta\epsilon i)}+1}$$

**Fermi-Dirac energy distribution for energies in the range E to E + dE**

The number of particles having energies in the range between E and E+dE is given by

$$n(E)\,dE = f(E)\,g(E)\,dE \qquad \text{---------- (1)}$$

where g(E) dE is the number of quantum states of energy between E and E +dE.

Sub. The expression for f(E) in eq. (1), then

$$n\,(E)dE = \frac{g(E)dE}{e^{\frac{Er-Ef}{kT}}+1} \qquad \text{---------- (2)}$$

For particles like electrons of spin angular momentum ±1/2 ħ, there are two possible spin orientation. For a system of such particles g(E) dE is given by

$$g\,(E)\,dE = 2 \times 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE$$

sub. the value of g (E) dE in eq. (2), get

$$n\,(E)\,dE = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{E^{\frac{1}{2}}\,dE}{e^{(E-E_F)/kT}+1} \qquad \text{------------- (3)}$$

This is Fermi-Dirac distribution law giving the number of particles with energies between E and E+dE.

**Fermi Energy**

The Fermi energy at absolute zero of temperature is denoted by $E_{Fo}$ and this is considered as a constant over a large range of temperature.

The Fermi function is, $f(E) = \frac{1}{e^{\left(E-E_{F0}\right)/kT}+1}$

At T=0, when E <$E_{Fo}$,

$$f(E) = \frac{1}{e^{-\infty}+1} = \frac{1}{0+1} = 1 \qquad \text{----------- (1)}$$

and at T = 0, when E> $E_{Fo}$,

$$f(E) = \frac{1}{e^{\infty}+1} = \frac{1}{\infty+1} = 1 \qquad \text{----------- (2)}$$

Equ. 1 and 2 shows that at T=0, the function f (E) is constant equal to 1 for all values of energies upto $E_{Fo}$ it falls to zero. That is at T=0, it is a step function.

Thus at absolute zero of temperature all possible quantum states of energy less than $E_{Fo}$ re occupied and all those of energy more than $E_{Fo}$ are empty.

Accordingly the Fermi energy $E_{Fo}$ is defined as the energy of the highest occupied level at absolute zero. At any other temperature T>0, when E= $E_{Fo}$, the Fermi energy is

$$f(E) = \frac{1}{e^{(E-E_{F_0})/kT}+1} = \frac{1}{e^{0/kT}+1} = 1/2$$

This means that at temperature T>0, the probability for occupation of a quantum states at the Fermi level is ½. At temperature T>0, 50% of the quantum states at the Fermi level are occupied and 50% are empty.

### Effect of temperature on Fermi Energy

The Fermi energy $E_F$ of an electron gas at temperature T is related to the value $E_{Fo}$ at T=0 by the equation

$$E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right]$$

It is seen that as T is increased $E_F$ decreases. But the rate of decrease with temperature is very small over a large range of temperature. The temperature at which $E_F$ becomes zero is very large. For free electrons in metallic copper this temperature is of the order of 90 x $30^3$K. So the temperature dependence of $E_F$ over practical range of temperature be neglected and $E_F$ at temperature T may be considered as constant equal to $E_F$.

### Energy distribution curve

The Fermi –Dirac energy distribution law is

$$n(E)dE = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\frac{E^{\frac{1}{2}}\,dE}{e^{(E-E_{Fo})/kT}+1} \qquad \text{---------- (1)}$$

(1) Curve at T = 0. At T = 0, when $E<E_{Fo}$, then

$$e^{(E-E_{Fo})/kT} = e^{-\infty} = 0$$

From eq. (1)

$$n(E)dE = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}dE$$

$$\text{or} \quad n(E) = CE^{1/2} \qquad \text{---------- (2)}$$

where C is constant.

At T = 0, when $E=E_{Fo}$, then

$$e^{(E-E_{Fo})/kT} = e^{\infty} = \infty$$

Therefore under this condition n(E) = 0.Thus the curve representing eq. (2) is a parabola which ends abruptly at E = $E_{Fo}$.

(2) Curve at T>0:

At T>0, when E<<$E_{Fo}$ the exponential term in the denominator of equ. (1) can be neglected in comparison with 1. So the region (E<<$E_{Fo}$) is the same parabola. Then as E approaches $E_{Fo}$, the curves falls towards the axis of E and intersects the line E=$E_{Fo}$ at the point P. When E>$E_{Fo}$ the curve approaches the axis asymptotically showing that at a higher temperature a few electrons have energy greater than $E_{Fo}$

**Fermi energy $E_{Fo}$ for free electrons in a metal**

The total number N of the free electrons in a metal of volume V is given by

$$N = \int_0^{\infty} n(E)\, dE$$

$$= \int_0^{\infty} f(E)\, g(E) dE$$

$$= \int_0^{E_{F_0}} f(E) g(E)\, dE + \int_{E_{F_0}}^{0} f(E) g(E)\, dE \quad \text{--------} \ (1)$$

At T = 0, when E≤$E_{F_0}$, then f (E) =1 and at T=0, when E≥$E_{F_0}$ then f(E) = 0. Hence in equ. (1) the second integral is zero and in the first integral f (E) = 1.

$$N = \int_0^{E_{F_0}} g(E)\, dE$$

$$= 4\pi V\, (2m/h^2)^{3/2} \int_0^{E_{F_0}} E^{1/2}\, dE$$

$$= 4\pi V\, (2m/h^2)^{3/2}\ \ 2/3\ E_{Fo}^{3/2}$$

$$= \frac{8\pi}{3} V \left(\frac{2mE_{F_0}}{h^2}\right)^{3/2}$$

From this equation,

$$\left(\frac{2mE_{F_0}}{h^2}\right)^{3/2} = 3N / 8\pi V$$

$$E_{F_0} = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \quad \text{--------} \ (2)$$

$$E_{F_0} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} \quad \text{--------} \ (3)$$

When n= N/V = no.of free electrons per unit volume, i.e.., the free electron density.

The values of $E_{Fo}$ calculated from eq. (3) for a number of metals are of the order of several electron volts. This fact is a very important difference between classical statistics and Fermi-Dirac statistics. According to classical statistics all electron in a metal at absolute zero would have zero energy.

## Fermi Temperature

The Fermi temperature $T_h$ is defined as the ratio of the Fermi energy $E_{Fo}$ at absolute zero to Boltzmann's constant k. Thus

$$T_F = E_{F0}/k \qquad \text{------ (1)}$$

*Relation between $T_F$ and the density of the free electron in a metal*

$$T_F = E_{F0}/k$$

$$= \frac{h^2}{2mk}\left(\frac{3n}{8\pi}\right)^{2/3}$$

$$= \frac{h^2}{2mk}\left(\frac{3}{8\pi}\right)^{2/3}(n)^{2/3}$$

Sub. the numerical value of h, m and k

$$T_F = \left(\frac{(6.63\ x\ 10^{-34})2}{2\ x\ 9.11\times10^{-31}\times1.38\times10^{-23}}\right) x \left(\frac{3}{8\pi}\right)^{2/3}(n)^{2/3}$$

$$= 4.23\ x\ 10^{-15}\ (n)^{2/3} \qquad \text{------ (3)}$$

*Relation between the degeneracy parameter A and $T_F$*

The degeneracy parameter A is $A = N/V\left(\frac{h^2}{2\pi mkT}\right)^{3/2}$ ---------- (4)

From eq. 2 the density n = N/V of the free electron is given by

$$n = N/V = 8\pi/3\left(\frac{2mkT}{h^2}\right)^{3/2} \qquad \text{----------- (5)}$$

Sub. this value in eq. (4)

$$A = \frac{8\pi}{3}\left(\frac{2mkT}{h^2}\right)^{3/2}\left(\frac{h^2}{2mkT\pi}\right)^{3/2}$$

$$= \frac{8}{3\sqrt{\pi}}(T_F / T)^{3/2} \quad = 1.5\ (T_F / T)^{3/2}$$

$$\text{Therefore } T_F / T = (A/1.5)^{2/3} \qquad \text{----------------- (6)}$$

This equation shows that the degeneracy condition that A>1 is equivalent to $T_F$>1

The value of $T_F$ for the free electrons in metal is very large. For the free electrons in copper $T_F$ $8.15\text{x}10^4$K. This value is much higher than room temperature so that the free electrons gas in copper is highly degenerate.

*Interpretation of the Fermi Temperature*

The temp. T of an ideal gas whose mean molecular K E is equal to the mean energy of the free electron in a metal at absolute zero is given by

$$3/2\ kT = U_0 = 3/5\ E_{Fo}$$

$$\text{Or } T = 2/5\ (E_{Fo}/k) = 2/5T_F$$

It means that if free electron gas is considered to obey the classical statistics a piece of copper would have to be heated to a temp. 2/5 times the Fermi temperature for the metal is

$$2/5 \times 8.15 \times 10^4 = 4.07 \times 10^4 k$$

**Thermionic Emission**

According to the Fermi-Dirac statistics the free electrons in the highest energy level in a metal at absolute zero have the Fermi energy $E_{Fo}$. But they are not emitted spontaneously from the metal because of attractive forces of other charges at the surface. Therefore, to enable an electron having maximum energy $E_{Fo}$ in the metal at zero K to escape from the surface to vacuum a certain minimum amount of energy $\Phi_o$ must be important to it. This energy is called the work function of the metal at 0K. At a higher temperature these energies are denoted by $E_F$ and $\Phi$.

On heating a metal to a high temperature T a free electron with energy $E_{Fo}$ may acquire an additional kinetic energy equal to the work function $\Phi$ of the metal. Then its total kinetic energy inside the metal is ($E_{F0}$ +$\Phi$). The electron with this K.E inside the metal will just escape into vacuum from the metal surface, and will have 0K.E. on emergence. Hence this energy is the P.E. of the electron at rest outside the metal. This P.E. is called surface barrier of the metal. It is denoted by $E_S$. Thus $E_S = E_{Fo} + \Phi$.

The Fermi-Dirac shows that if a metal is heated to a high temperature only those electron in the shaded portion of the curve will have K.E. > than Es and hence they can escape from the metal surface. Thus when a metal is heated to a high temperature T a free electron will occur total K.E. > surface barrier potential energy Es will be emitted from the metal. This phenomenon is called thermionic emission.

**Richardson – Dushmann Equation**

Let $E_x$ be the total K.E of an electron at temperature T in the positive x-direction. An electron having x-components of its velocity in the range between $\nu_x$ and $\nu_x + d\nu_x$ will escape from the metal surface in the positive x-direction if $\frac{1}{2} m\nu_x^2 \geq Es$.

$$\text{If } E_x \geq Es$$

$$\text{Or } E_x \geq E_{Fo} + \Phi \qquad \text{---------------- (2)}$$

The number of electrons per unit volume with the x-component of their velocity in the range $\nu_x$ and $\nu_x + d\,\nu_x$ is $\frac{n\,(\nu_x) d\nu_x}{V}$

The number of such electrons escaping from the metal surface per unit area per second is

$$\frac{\nu_x n\,(\nu_x) d\nu_x}{V}$$

The current density dJ due to these electrons that is the current per unit area i.e., the charge passing normally through unit area per second is given by

$$dJ = \frac{q\,\nu_x n\,(\nu_x) d\nu_x}{V} \qquad \text{--------(3)}$$

where q – electronic charge. The total current density J is given by

$$J = \frac{q}{V} \int_{E_x = E_s}^{\infty} \nu_x n\,(\nu_x) d\nu_x \qquad \text{----------- (4)}$$

The function $n\,(\nu_x) d\nu_x$ is given by Fermi-Dirac law of distribution of velocity in the x-direction

$$n\,(\nu_x) d\nu_x = V\left(\frac{4\pi m^2 kT}{h^3}\right) e^{E_{F_0}/kT} . e^{\frac{-m\nu_x^2}{2kT}}\, d\nu_x$$

In this equation, we sub. $\frac{1}{2} m\nu_x^2 = E_x$

$$m(\nu_x)d\nu_x = dE_x$$

$$d\nu_x = 1/m\nu_x \, dE_x$$

$$\text{Hence, } n\,(\nu_x)d\nu_x = V\left(\frac{4\pi m^2 kT}{h^3}\right) e^{E_{F_0}/kT} . e^{\frac{-E}{kT}} \,(1/m\nu_x)dE_x$$

Or
$$\nu_x n\,(\nu_x)d\nu_x = V\left(\frac{4\pi mkT}{h^3}\right) e^{\frac{E_{F_0}}{kT}} . e^{\frac{-E}{kT}} \, dE_x$$

Sub. this equation in equ. (4)

$$J = q\left(\frac{4\pi mkT}{h^3}\right) e^{\frac{E_{F_0}}{kT}} \int_{Es}^{\infty} e^{\frac{-Ex}{kT}} dE_x \quad \text{--------} (6)$$

The value of the integral is

$$\int_{Es}^{\infty} e^{\frac{-Ex}{kT}} dE_x = \left[-kTe^{\frac{-Ex}{kT}}\right]^{\infty}_{Es}$$

$$= kTe^{\frac{-Es}{kT}}$$

$$= kTe^{-(E_{Fo} + \Phi)/kT} \quad \text{--------} (7)$$

Sub. this value in eq. (6) and simplifying

$$J = \left(\frac{4\pi k^2 mq}{h^3}\right) T^2 e^{-\Phi/kT} \quad \text{--------} (8)$$

which is written as $J = A_0 T2^2 e^{-\Phi/kT}$ -------- (9)

Where $A_0 = \left(\frac{4\pi k^2 mq}{h^3}\right)$ = universal constant = $1.204 \times 10^6$ A/m$^2$K$^2$

Eq.(9) is known as Richardson's or Dushman's or the Richardson- Dushmann equation. It was first derived by O.W. Richardson in 1901 and later the theory of its derivation were perfected by S.Dushman in 1923.

The eq. is based on the assumption that all the electrons having energy equal to or greater than the surface potential barrier or emitted but quantum mechanical theory shows that an electron having energy $E_x \geq E_s$ may not escape from the metal surface it may be reflected back, and that the probability of escape for such an electron is (1-r) where r is the reflection coefficient which is a function of$(\nu_x)$. But in thermionic emission velocity range of the emitted electron is not large, in this process r can be considered as constant over the small velocity range.

$$J = A_0(1-r)T^2 e^{-\Phi/kT} \quad \text{----------------------}(10)$$

## Comparison of M-B, B-E and F-D Statistics

| Quantity | M-B | B-E | F-D |
|---|---|---|---|
| Particles | Distinguishable | Indistinguishable called bosons | Indistinguishable called Fermions |
| Spin | - | 0,1,2,------- | ½, 3/2, 5/2, ------ |
| Wave function | - | Symmetric under interchange of two bosons | Antisymmetric under interchange of two bosons |
| Number of particles per energy state | No upper limit | Bosons don't obey Pauli exclusion principle: No upper limit to the no. of particles per quantum state. | Fermions obey Pauli exclusion principle: Max. of one particles per quantum state. |
| Distribution function f(E) | $\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} e^{-E/kT}$ | $\frac{1}{e^{\alpha}e^{\frac{E}{kT}} - 1}$ | $\frac{1}{e^{\frac{(E-Ef)}{kT}} + 1}$ |

**Possible Questions**

1. Give three differences between M-B, F-D and B-E statistics.
2. Explain Bose temperature and Bose-Einstein condensation
3. Which kind of particles is called as fermions?
4. What is called Bose- Einstein condensation?
5. Derive Richardson Dushmann equation.
6. Define Fermi energy.
7. Define the term Bose temperature.
8. What are called fermions?
9. Obtain Planck's law of radiation from Bose- Einstein distribution law.
10. Explain energy distribution curve of FD statistics.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**

**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT IV (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | B.E distribution law is used to derive ____________of radiation | Planck's law | Weiss law | Widemann Franz law | Rayleigh's law | Planck's law |
| 2 | Wave function of the system of identical Bosons is | asymmetric | linear | non-linear | symmetric | symmetric |
| 3 | The variable W in an equilibrium stands for | minimum probability distribution | probability distribution | maximum probability distribution | constant probability distribution | maximum probability distribution |
| 4 | Which of the following obey Pauli exclusion principle? | M.B. statistics | B.E. statistics | F.D. statistics | Einstein’s equation | F.D. statistics |
| 5 | Which of the following do not obey Pauli exclusion principle? | M.B. statistics | B.E. statistics | F.D. statistics | Einstein’s equation | B.E. statistics |
| 6 | In B.E. distribution, the constant $e^{\alpha}$ must be __________ | greater than 1 | smaller than 1 | equal to 1 | zero | greater than 1 |
| 7 | The molecule of an ordinary gas have spin angular momentum equal to an integral multiple of _________ | h | ħ/2π | Ћ | h/2π | ħ |
| 8 | The molecules obey B.E. statistics are ____________ | photons | phonons | fermions | bosons | bosons |
| 9 | _________ is the energy distribution | f(E) | g(E) | n(E) | f | f(E) |

| | | | | | | |
|---|---|---|---|---|---|---|
| | function. | | | | | |
| 10 | ____________ is the number of quantum states | f(E) | g(E) | n(E) | f | g(E) |
| 11 | In B.E. energy distribution, if $e^{\alpha} = 1$, for E=0, then n(0) dE = | postive infinity | negative infinitive | 1 | 0 | postive infinity |
| 12 | In B.E. energy distribution, if $e^{\alpha} < 1$, for E=0, then n(0) dE = | postive infinity | negative infinitive | 1 | 0 | negative infinitive |
| 13 | For an ideal B.E. distribution the degeneracy parameter A cannot be ___________- | greater than 1 | smaller than 1 | equal to 1 | zero | greater than 1 |
| 14 | For all known B.E. gases, $T_B$ is very _______ | high | low | small | 0 | low |
| 15 | The value of Reimann Zeta function is ______ | 6.212 | 1.612 | 2.126 | 2.612 | 2.612 |
| 16 | A gaseous phase consisting of Ne molecules distributed among the energy states ____ than the ground state. | higher | lower | equal to | very smaller | higher |
| 17 | The transition of liquid $_2He^4$-I to superfluid liquid $_2He^4$-II is observed at _________ | 8.12 K | 2.18 K | 1.82 K | 1.28 K | 2.18 K |
| 18 | For an ideal B.E. gas the condensation temperature is $T_B$. Find the temperature at which the number of molecules in the zero energy state (E=0) is 7/8 times the total number of molecules in the gas. | $T=T_B$ | $T=4T_B$ | $T=1/4\ T_B$ | $T=4/3\ T_B$ | $T=1/4\ T_B$ |
| 19 | E.Fermi developed the statistics for _______ | photons | bosons | phonons | electrons | electrons |
| 20 | At T=0, when $E<E_{F0}$, the Fermi energy is given by ________ | one | infinity | negative infity | zero | one |
| 21 | At T=0, when $E<E_{F0}$, the Fermi energy is given by ________ | one | infinity | negative infity | zero | zero |
| 22 | For free electrons in metallic copper the temperature is of the order of | $90 \times 10^3$ K | $90 \times 10^{-3}$ K | $90 \times 30^3$ K | $90 \times 30^{-3}$ K | $90 \times 30^3$ K |

| | | | | | | |
|---|---|---|---|---|---|---|
| | _________ | | | | | |
| 23 | For free electrons in copper, $T_F$ = ________ | 8.15 x $10^2$K | 8.15 x $10^{-2}$ K | 8.15 x $10^{-4}$ K | 8.15 x $10^4$K | 8.15 x $10^4$K |
| 24 | The value of $T_F$ free electrons in a metal is _____ | very large | very small | zero | infinity | very large |
| 25 | The free electron gas in copper is _______ | highly degenerate | degenerate | weekly degenerate | non-degenerate | highly degenerate |
| 26 | Surface potential barrier energy of the metal is denoted by ________________ | $E_P$ | $E_S$ | S | $S_E$ | $E_S$ |
| 27 | Richardson explain his theory in the year ______ | 1801 | 1701 | 1901 | 1921 | 1901 |
| 28 | Spin value of bosons are in the order of _________ | 0,1,2,……. | 0, 2,4,6,……….. | ½, 3/2, 5/2,…… | 1/3, 3/3, 5/3,………… | 0,1,2,……. |
| 29 | S.Dushmann explained his theory in the year _______ | 1801 | 1701 | 1923 | 1921 | 1923 |
| 30 | Spin value of fermions are in the order of _________ | 0,1,2,……. | 0, 2,4,6,……….. | ½, 3/2, 5/2,…… | 1/3, 3/3, 5/3,………… | ½, 3/2, 5/2,…… |
| 31 | The value of b is given by | 3 KT | KT | 1/KT | 4KT | 1/KT |
| 32 | In B.E statistics the particles are identical and indistinguishable. These particles are called as | Bosons | fermions | leptons | baryons | Bosons |
| 33 | Particles with half-integral spin are called as | Bosons | fermions | leptons | baryons | fermions |
| 34 | Fermions obey ______________principle | Heisenberg | Le-chatlier | Pauli | Haber | Pauli |
| 35 | Condition for B.E distribution to approach M.B distribution is $1/A(e^{bE}) >> 1$ i.e | A<=1 | A<<1 | A>>1 | A>>1 | A<<1 |
| 36 | In B.E statistics the particles are identical and indistinguishable. These particles | Bosons | fermions | leptons | baryons | Bosons |
| 37 | The Bosons has | spin 1 | zero or half- | zero or whole | zero | zero or half- |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  |  | integral spin | number |  | integral spin |
| 38 | The examples for Bosons | photons | electrons | neutrons | protons | photons |
| 39 | Particles with half-integral spin are called as | bosons | Fermions | leptons | electrons | leptons |
| 40 | The examples for Fermions | Photons | phonons | electrons | antiparitcles | electrons |
| 41 | The spin of the photon is | 0 | 1 | 2 | ½ | 1 |
| 42 | In F.D statistics the particles are identical and indistinguishable. These particles | Fermions | bosons | photons | kryptons | Fermions |
| 43 | B.E distribution function is given by | {1/( ea + bE) } | {1/( ea + bE) + 1} | {( ea + bE) – 1} | {1/( ea + bE) – 1} | {1/( ea + bE) – 1} |
| 44 | Fermi energy Ef = | - aKT | aKT | –1/ aKT | 1/ aKT | - aKT |
| 45 | Fermi-Dirac distribution function FD(E) = | {1/( ea + bE) + 1} | {1/( ea + bE) - 1} | {1( ea + bE) - 1} | {-1/( ea + bE) + 1} | {1/( ea + bE) + 1} |
| 46 | In terms of Fermi energy F.D distribution function is fFD(E) = | {-1/( eE + EF) + 1} | {1/( eE - EF) + 1} | {1/( eE + EF) + 1} | {1/( eE + EF) - 1} | {1/( eE + EF) + 1} |
| 47 | When T = 0 and E < Ef , then fFD(E) = | 0 | 1 | ½ | 3 | 1 |
| 48 | The degeneracy parameter e-a = | N/V ( h2 / 2pmkt )1/2 | N/V ( h2 / 2pmkt )3/4 | N/V ( h2 / 2pmkt ) | N/V ( h2 / 2pmkt )3 | N/V ( h2 / 2pmkt )3 |
| 49 | The maximum value of degeneracy parameter in B.E statistics is | One | two | three | Four | One |
| 50 | B.E statistics is used to find the ___________among identical | energy distribution | frequency distribution | both a and b | mass distribution | energy distribution |
| 51 | According to B.E distribution law the number of Bosons having energies | g(E)dE/{( ea + bE) + 1} | g(E)dE/{( ea + bE) – 1} | g(E)dE/{( ea + bE) – 1} | g(E)dE/{( ea + bE) – 1}1/2 | g(E)dE/{( ea + bE) – 1}1/2 |
| 52 | According to Plank's law of radiation, the energy of the photon is | Constant | same | not distinct | Vary | Constant |
| 53 | For an isolated system the total energy in a B.E. distribution law is used to derive ________ of radiation | A<=1 | A<<1 | A>>1 | A=1 | A<<1 |
| 54 | Wave function of the system of identical Bosons is | Unsymmetric | linear | symmetric | Anti symmetric | symmetric |

| | | | | | | |
|---|---|---|---|---|---|---|
| 55 | The molecule of an ideal B.E gas in two phases at | T = TB | T > TB | T < TB | T <= TB | T < TB |
| 56 | The ___________consists of no molecules occupying ground state | condensed phase | liquid phase | gaseous phase | inert gas | gaseous phase |
| 57 | ___________of same energy can have two different directions of polarization | Planck’s law | Weiss law | Franz law | Newtons law | Planck’s law |
| 58 | At ____________the molecule just reach the zero energy state | Bohr temperature | Kelvin temperature | Neel temperature | Curie temperature | Bohr temperature |

**Applications of Quantum Statistical Mechanics:** Ideal Bose gas: Photons − Black body and Planck radiation − Photons − Specific heat of solids − Liquid Helium.

Ideal Fermi gas: Properties − Degeneracy − Electron gas − Pauli paramagnetism

Ferromagnetism: Ising and Heisenberg models.

## EMISSIVE POWER

The emissive power $e_\lambda$ of a body at a given temperature for radiant energy of wavelength λ is defined as the energy emitted per unit area per seconds per unit range of wavelength $\frac{b}{n}$ λ & λ+d λ at the given temperature.

unit→1 Walt per square meter per Angstrom.

## ABSORPTIVE POWER ($a_\lambda$)

The absorptive power $a_\lambda$ of a body at a given temperature for radiant energy of wavelength λ is the ratio of radiant energy of wavelength λ is absorbed per unit area per second, by the body at the given temperature to the radiant energy of the same wavelength incident on unit area per second at the temperature.

For perfectly black body $a_\lambda=1$.

## Kirchoff"s law of Radiation

The law states that the ratio of the emissive power $e_\lambda$ of a body for any wavelength at a given temperature to its absorptive power $a_\lambda$ for the wavelength at the temperature is constant and is equal to the emissive power $E_\lambda$ of a perfectly black body at that temperature.

$$=E_\lambda$$

## Black Body Radiation

A body which completely absorbs radiation of all wavelength incident on it is called *perfectly black body*. Since a good absorber of radiation is also a good emitter of radiation , a perfectly black body is the best possible emitter at any given temperature .The radiation emitted by such kind of body is called black body radiation, or full radiation or temperature radiation.

A perfectly black body is an ideal conception. There is no known surface which can be regarded as perfectly black. Lamp black or platinum black is the nearest approach to the perfectly black body. Lamp black can absorb about 96% of the radiant energy incident on it, &platinum black absorbs about 98%. In practice almost perfectly black body consist of a double-walled hollow metal sphere. The sphere has a small hole O. There is conical projection P opposite the hole. The inner surface of the sphere is coated with lamp black .The space between the wall is evacuated to prevent loss of heat by conduction or convention .when any radiant energy enters the space through the hole, it suffers multiple reflections. At each reflection about 96% of the incident radiant energy is absorbed .hence after few reflections all the radiant energy is absorbed by the sphere. The function of the conical projection is to prevent direct reflection of the radiant energy from the surface opposite to the hole. The hole O in the sphere acts as a perfectly black body because it absorbs all the radiant energy incident on it. When the sphere is heated black body radiation is emitted from the hole.

## Liquid Helium

As an application of B-E. statistics, the qualitative nature of the superfluid transition of liquid helium at 2.2 K were investigated. Ordinary helium consists almost entirely of neutral atoms of the isotope $_2He^4$. As the total angular momentum of this atom is 0.

Helium exhibits peculiar properties at low temperatures.

(i) Helium gas at atmospheric pressure condenses at 4.3 K into a liquid of very low density about 0.124 gm / cm$^3$

(ii) Further cooling about 0.82 K doesnot freeze it and its believed that it remains all the way down to absolute 0. The solid state of helium does not form unless it is subjected to an external pressure of atleast 23 atm.

(iii) For He$^1$ in liquid phase there is another phase transition called λ transition which divides the liquid state into two phases He I and II. K. Onnes while liquefying helium noted that about 2.2 K, density appeared to pass through abrupt maximum and then decreasing slightly. Investigations also revealed that critical temperature at 2.186 K. It represents a transition to a new state of matter known as liquid He II.

a) Heat conductivity is very large in the order of $3.10^6$ times greater.

b) Co-efficient of velocity gradually diminishes as the temperature is lowered and appears to be approaching 0 at absolute 0 temp.

c) Specific heat measurements by Kessom show that specific heat curve is discontinuous at 2.186 K. The shape of the specific heat curve resembles the shape of the letter λ and this peculiar transition is called λ transition and the discontinuity temp. 2.186 K is called λ point. Kesson concluded that transition He I →He II at $T_\lambda$ is second order transition. The transition temp. decreases as the pressure is increased.

**Degeneracy**

(i) **Weak degeneracy:** At $T > T_F$ (i.e., at intermediate temperatures) the Fermi gas is said to be slightly degenerate. In this case $kT > \in_F (0)$, then $\in_F$ is negative or α is positive and $A < 1$.

For $A < 1$, we can write

$$\frac{1}{\frac{1}{A}e^{\alpha}+1} = \left(\frac{1}{A}e^{\alpha}+1\right)^{-1} = Ae^{x}(1+Ae^{-x})^{-1}$$

$$=Ae^{-x}(1-Ae^{-x}+a^{2}e^{-2x}-\ldots\ldots.)$$

$$\text{Therefore, } f_1(x) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} x^{1/2}\,dx / \frac{1}{A}e^{\alpha}+1$$

$$= \frac{2}{\sqrt{\pi}}\left[A\int_0^{\infty} e^{-x}x^{1/2}dx - A^2\int_0^{\infty} e^{-x}x^{1/2}dx - A^3\int_0^{\infty} e^{-x}x^{1/2}dx - \ldots\ldots\right]$$

$$=A-A^2/2^{3/2}+A^3/3^{3/2}-\ldots\ldots\ldots\ldots \quad (1)$$

$$\text{Similarly, } f_2(\alpha)= A = A^2/2^{5/2}+A^3/3^{5/2}-\ldots\ldots\ldots\ldots \quad (2)$$

Using these values of $f_1(\alpha)$ and $f_2(\alpha)$, equations (10) and (12) take the form

$$n = g_s\, .\, V/h^3\,(2\pi mkT)^{3/2}\,[A-A^2/2^{3/2}+A^3/3^{3/2}] \quad \text{-----------} (3)$$

$$E = 3/2\, g_s\, .\, V/h^3\,(2\pi mkT)^{3/2}\,[A-A^2/2^{3/2}+A^3/3^{3/2}] \quad \text{-----------} (4)$$

Dividing eq. (4) by (3),

$$E/n = 3/2\, kT\,[1+A^2/2^{5/2}-A^3/3^{5/2}] \quad \text{-------------} (5)$$

To the first approximation We can write

$$n = g_s\, .\, V/h^3\,(2\pi mkT)^{3/2}\,A$$
$$E = 3/2\, g_s\, .\, V/h^3\,(2\pi mkT)^{3/2}\,kT.A$$
$$E/n = 3/2\,kT \text{ or } E = 3/2\,nkT \quad \text{-------------} (6)$$

which is well known relation for a perfect gas in classical statistics.

A comparison of equations (5) and (6) shows that ideal Fermi-Dirac gas deviates from perfect gas behaviour and this derivation is called degeneracy. It is obvious that degeneracy is the function of A. Greater is the value of A, more marked will be the degeneracy. Hence for $A<1$or $T>T_F$, the Fermi gas slightly degenerate.

**Case (ii) strong degeneracy.** When α is large and negative $A=e^{-\alpha} >>1$. As degeneration increases will increases of A, therefore in this case degeneracy becomes more prominent. Further to the first approximation; from en. (3)

$$A \approx 1/g_s \,.\, n/V\, h^3/(2\pi mkT)^{3/2}$$

This eqn. shows that the gas will be strongly degenerate at low temperature and high particles densities n/v. The evaluation of integrals $f_1(\alpha)$ and $f_2(\alpha)$ under these conditions is complicated.

This case of strong degenerate at low temperature ranges:

(a) At absolute zero i.e when T= 0
(b) When T is above absolute zero, but A>> 1.

**Case (a) At absolute zero i.e. when T=0.** When T →0 A→0. In this case the Fermi-dirac gas is completely degenerate.

At T=0,

$$f(\in) = \frac{1}{\frac{1}{A}e^{\epsilon/kT}+1} = \frac{1}{e^{\frac{(\epsilon-\epsilon_F)}{kT}}+1} = 1 \text{ for } 0 \leq \epsilon \leq \epsilon_F(0)$$

$$= 0 \text{ for } \epsilon > \epsilon_F(0)$$

where $\epsilon_F(0)$ is given by eqn. (18)

Now the **total internal energy of perfect Fermi- dirac gas at** T=0 **i.e. zero point energy of Fermi gas is**

$$E_0 = 3nh^2/10m\,[3n/4\pi Vg_s]^{2/3} = 3/5\, n\, \epsilon_F\,(0) \qquad \text{---------- (8)}$$

Now the pressure at T=0 is given by

$$P_0 = 1/3\, E_0/V$$
$$= 1/5nh^2/V_m\,(3n/4\pi g_s V)^{2/3} \qquad \text{--------- (9)}$$

Form equations (8) and (9) it is obvious that a strongly degenerate Fermi-dirac gas possesses energy and exerts a pressure even at 0K, quite unlike a Bose Einstien and classical gases where the energy and pressure at absolute zero are zero.

**Case (b) At temperature above absolute zero :but A> >1or T<<Tf**

In this case the Fermi –gas is strongly degenerate at low temperature and $\epsilon$ is still positive. From equation (17) the number of particles lying in the energy range between $\epsilon$ and $\epsilon$+d$\epsilon$ is given by

$$dn\,(\epsilon) = f(\epsilon)d(\epsilon) = 3/2\, n/[\,\epsilon_F\,(0)]^{3/2}.\, \epsilon^{1/2} d\,\epsilon/e^{(\epsilon-\epsilon F)/kT}+1 \qquad \text{-------(10)}$$

Therefore, the total number of particles is

$$n = \int_0^\infty dn(\epsilon) = 3/2\, n/[\,\epsilon_F(0)]^{3/2} \int_0^\infty \quad \epsilon^{1/2} d\,\epsilon/e^{(\epsilon-\epsilon F)/kT}+1 \qquad \text{----------- (11)}$$

and the total integral energy is

$$E = \int_0^\infty \epsilon dn\,(\epsilon) = 3/2\, n/[\,\epsilon_F(0)]^{3/2} \int_0^\infty \quad \epsilon^{1/2} d\,\epsilon / e^{(\epsilon-\epsilon F)/kT} + 1 \qquad \text{------------ (12)}$$

To solve the integrals in equations (31) and (32), let us consider the general integral of the type

$$I = \int_0^\infty \emptyset \frac{(\epsilon)d\epsilon}{e^{\frac{\epsilon-\epsilon_F}{kT}}} + 1 \qquad \text{----------- (13)}$$

Where $\emptyset(\epsilon)$ is a simple function of such that Ø( ) =0 when =0.

The integral of eqn. (33) can be expanded using the method of taylor's series expansion,

Where Ø', Ø''' etc. denote the first, third etc. differentials of the function Ø.

Now for $\Phi(\epsilon) = \epsilon^{1/2}$ --------- (15)

$$\epsilon_F / \epsilon_F\,(0) = [1+1/8(\pi kT/\,\epsilon F)^2 + 7/640\,(\pi kT/\,\epsilon_F)^4 + \,]^{-2/3} \qquad \text{---------- (16)}$$

Remembering that kT < < f,we can take into account only the first two terms in the bracketed expression and write

$$\epsilon_F/\,\epsilon_F\,(0) = [1+1/8(\pi kT/\,\epsilon F)^2]^2 \approx 1-1/12\,(\pi kT/\,\epsilon F)^2 \qquad \text{--------- (17)}$$

This gives

$$1/\,\epsilon_F^2 \approx 1/[\,\epsilon_F\,(0)]^2\,[1+1/6\,(\pi kT/\,\epsilon F)^2] \qquad \text{------------ (18)}$$

Now make the crude approximation by putting f= f(0) in the second term of above expression

$$1/\,\epsilon_F^2 \approx 1/[\,\epsilon_F\,(0)]^2\,[1+1/6\,(\pi kT/\,\epsilon_F(0)^2] \qquad \text{----------- (19)}$$

Now using equation (19), equation (17) gives

$$\epsilon_F \approx \epsilon_F\,(0)\,[1-1/12\,(\pi kT/\,\epsilon_F(0))^2] \qquad \text{------------ (20)}$$

$$E \approx n\,\epsilon_F\,(0)\,(\epsilon F\,/\epsilon_F\,(0)^{5/2} \quad [1+5/8\,(\pi kT/\,\epsilon_F)^2]$$

Now using equations (39) and (40),we get

$$E \approx 3/5\, n\,\epsilon_F\,(0)\,[1+5/12(\pi kT/\,\epsilon_F\,(0)] \qquad \text{----------- (22)}$$

The corresponding pressure is

$P = 2/3\ E/V \cong 2/5\ (n\, \epsilon_F\ (0)/V)\ [1+5/12\ (\pi kT/\ \epsilon_F\ (0)^2]$ ------------- (23)

Equations (22) and (23) represent the approximate energy and pressure of a strongly degenerate gas.

**Electron Gas**

A metal can be considered to be composed of a system of fixed positive nuclei and a no. of mobile electrons referred to us the electron gas.

To study the properties of an electron gas at low temperature in the region. For electrons s=1/2 so $g_z = 2s+1 = 2$.

$\varepsilon_f = h^2/2m \left(\frac{3n}{4\pi .V.2}\right)^{2/3}$

$= h^2/8m \left(\frac{3n}{\pi .2}\right)^{2/3}$ ----- (1)

$E_a = 3/5\ n\ \varepsilon_f$ ----------- (2)

In the limit T → 0 Which means that in the limit every one of the states is occupied fully up to the energy level $\varepsilon_f$ whereas all the states above this energy level are empty. For electrons $m = 9.1 \times 10^{-28}$gm, and g =2.

$$\frac{1}{D} = \frac{h^2}{2\ x\ 9.1\ x\ 10^{-28}\ kT}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

A typical metal atomic weight 100 and density 10 so that the volume of gm. atom of 10cc. and the number of electrons assuming one free electron from atom is $6.02 \times 10^{23}$. Then

$$\frac{1}{D} = \frac{(6.62\ x\ 10^{-27})^2}{2\ x\ 9.1\ x\ 10^{-28}\ x\ 1.38\ x\ 10^{-18}\ x\ T}\left(\frac{3x\ 6.02\ x\ 10^{23}}{8\ x\ 3.14\ x\ 10}\right)^{2/3}$$

$$= 10^5/\ 1.5T$$

Which means degeneracy is sufficiently high. It shows clearly that for electron gas, a classical statistics is not valid and can be applied only at temperature of the order of $10\ ^5$K. Therefore at low and other ordinary working temperatures, it is necessary to use Fermi- Dirac statistics to study the electron gas in the metals. At low temperature electronic contribution to the specific heat of metals is given by the equ.

$$C_v = \tfrac{1}{2}\ nk\ \pi^2\ (kT/\ \varepsilon_f)$$

$$D = (kT/\ \varepsilon_f)$$

$$C_v = \frac{1}{2} nk \pi^2 D$$

Using this value find the value of 1/D,

$$C_v = \frac{1}{2} nk \pi^2 \times 1.5 \times 10^{-5} \times T$$

Sub. nk = R

$$= 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$= 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$\pi^2 = 10$$

$$C_v = \frac{1}{2} \times 1.5 \times 10^{-5} \times 2 \times 10 \times T$$

$$= 1.5 \times 10^{-4} \times T \text{ cal/gm. atom}$$

Pressure of the electron gas can be obtained by,

$$P_o = \frac{2}{5}\frac{n\varepsilon f}{V}$$

$$= \frac{2}{5V}\frac{h^2}{2m}\left(\frac{3n}{4\pi V gs}\right)^{2/3}$$

$$= \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3} \text{ using } gs = 2$$

For a metal of atomic weight 100 and density 10

$$P_o \tilde{} 10^5 \text{ atoms}$$

Which means at normal temperature the pressure of gas is sufficiently high.

**Ising and Heisenberg Model**

Transition of non-ferromagnetic state into ferromagnetic state is called phase transition, in this transition, the state of the body changes continuously.

Consider a ferromagnetic substance, like iron and nickel. Without any external field being applied, some of the spins of the atoms become spontaneously polarized in the same direction, below curie temperature Tc. This create a macroscopic magnetic field. The spontaneous magnetization, created vanishes if temperature is greater than Tc, because thermal energy makes some of the aligned spin to flip over. Thus spins get oriented at random no net magnetic field is produced. As the curie temperature approached both sides of the specific heat of the metal approaches infinity. The transition from non-ferromagnetic to the ferromagnetic state, called the phase transition, is associated with some kind of change in the symmetry of the lattice; For example the ferromagnetism symmetry of the spins is involved. In Ising model the system considered is the array of N fixed points called lattice sites that from an n-dimensional periodic lattice (n=1,2,3). Associated with each lattice site is a spin variable, $s_i$, i =1 to n, It is a number that either +1 or -1. There is no other variable. If $s_i = +1$ the ith state is said to have spin up and $s_i = -1$, it is said to have spin down. A given set of $\{s_i\}$specifies a configuration of the whole system, whose energy is defined to be

$$E_1\{s_i\} = -\sum_{\langle i,j\rangle} \in_{ij\ s_i} si\ sj - \mu H \sum_{i=1}^{N} si \qquad \text{------------- (1)}$$

Where the subscript I stands for Ising and the symbol $\langle i,j\rangle$ denotes a nearest-neighbour pari of spins. There is no distinction between $\langle i,j\rangle$ and $\langle j,i\rangle$ is the interaction energy μH interaction is associated with the external magnetic field H. For spontaneous magnetization H= 0. $\in_{ij}$ and H are given constants. Applied the model to the case is isotopic interaction so that all $\in_{ij}$ have the same value ∈. For energy

$$E_1\{s_i\} = -\in \sum_{\langle i,j\rangle} \quad si\ sj - \mu H \sum_i si \qquad \text{--------- (2)}$$

The case ∈ > 0 corresponds to ferromagnetism and the case ∈< 0 to antiferromagnetism. In the former case neighbor spins tend to be parallel while in the latter case they tend to be antiparallel. In eq. (2) the sum over $\langle i,j\rangle$ contains N/2 terms where is the number of nearest neighbors of any given site. In the Ising model eq. 2, geometry of the lattice enters through and interaction energy $\in_{ij}$

Consider only these case ∈ > o. The partition function is

$$Z = \sum_{S1} \sum_{S2} \sum_{SN} e^{-\beta E1\ \{Si\}}$$

### Possible Questions

1. Define specific heat capacity at constant volume.
2. Explain Ising and Heisenberg model.
3. Discuss about specific heat of solids.
4. What are called photons?
5. State Dulong and Petit's law.
6. Give a note on liquid helium.
7. Define degeneracy.
8. Give a note on pauli paramagnetism.
9. What are the applications of quantum statistical mechanics?
10. State Kirchhoff's law.
11. Write a note on black body and Planck radiation law.

# KARPAGAM ACADEMY OF HIGHER EDUCATION

**Coimbatore-641021.**

**(For the candidates admitted from 2018 onwards)**

## DEPARTMENT OF PHYSICS

## UNIT V (Objective Type/Multiple choice Questions each Questions carry one Mark)

## THERMODYNAMICS AND STATISTICAL MECHANICS

## PART –A(Online Examination)

| S.No. | QUESTIONS | OPTION 1 | OPTION 2 | OPTION 3 | OPTION 4 | ANSWER |
|---|---|---|---|---|---|---|
| 1 | In solid heat is transferred by __________ | Conduction | convection | radiation | Irradiation | Conduction |
| 2 | In liquid heat is transferred by __________ | Conduction | convection | radiation | Irradiation | convection |
| 3 | Conduction and convection cannot take place in ___________ | solid | liquid | inert gas | empty space | empty space |
| 4 | _______________ does not require any material medium. | Conduction | convection | radiation | Irradiation | radiation |
| 5 | Radiant energy is also called as ____ | latent heat | radiant heat | entropy | enthalpy | radiant heat |
| 6 | The wavelength of infrared ranges from _________ | 7500Å to 1000000Å | 750Å to 100000Å | 7500Å to 10000Å | 750Å to 1000000Å | 7500Å to 1000000Å |
| 7 | _____________ travels with speed of light. | Conduction | convection | radiation | Irradiation | radiation |
| 8 | The nature of radiant energy is same as that of ________ | sound | heat | light | electricity | light |
| 9 | The radiant energy emitted depends on __________ | temperature | material | volume | height | temperature |
| 10 | For a black body the emissive power is denoted by ___________ | E | λ | λE | Eλ | E |
| 11 | Unit of emissive power is _________ | 1 W/m | 1WmÅ | 1WÅ | 1W/m2Å | 1W/m2Å |
| 12 | For a perfectly black body aλ = _________ | 0 | ∞ | 1 | -∞ | 0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 13 | Absorptive power is represented by _____ | a | λ | λa | aλ | aλ |
| 14 | Kirchoff’s law of radiation = | eλ/aλ = Eλ | eλ/aλ = λ | aλ/eλ = Eλ | eλ/Eλ = aλ | eλ/aλ = Eλ |
| 15 | ____________ black is nearest approach to a perfectly black body. | gold | platinum | diamond | silver | gold |
| 16 | Which is considered as a perfect absorber as well as a perfect emitter? | Gray body | Black body | Real body | White body | Black body |
| 17 | Which body that emits a constant emissivity regardless of the wavelength? | Gray body | Black body | Real body | White body | Gray body |
| 18 | At same temperatures, the radiation emitted by all real surfaces is ______ the radiation emitted by a black body. | Less than | Greater than | Equal to | Either less than or greater than | Less than |
| 19 | Which is NOT a characteristic of emissivity? | It is high with most nonmetals | It is directly proportional to temperature | It is independent with the surface condition of the material | It is low with highly polished metals | It is low with highly polished metals |
| 20 | What is the emissivity of a black body? | 0 | 1 | 0.5 | 0.25 | 1 |
| 21 | What is the absorptive of a black body? | 0 | 1 | 0.5 | 0.25 | 0 |
| 22 | Above Curie point | A ferromagnetic material becomes paramagnetic | a ferrite becomes an insulator | a insulating material becomes a ferrite | a diamagnetic material becomes a paramagnetic material | A ferromagnetic material becomes paramagnetic |
| 23 | Which of the following is a paramagnetic material? | Palladium | Lead | Pure Iron | Bismuth | Lead |
| 24 | Which of the following is a ferromagnetic material? | Palladium | Lead | Iron | Bismuth | Iron |
| 25 | All of the following materials are Ferromagnet except | Nickel | Bismuth | Silicon | Mild steel | Mild steel |
| 26 | By adding silicon to ferromagnetic , materials | electrical resistivity increases and also magnetic | electrical resistivity decreases and also magnetic | electrical resistivity decreases and magnetic | electrical resistivity increases and magnetic | electrical resistivity decreases and magnetic permeability |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | permeability increases | permeability decreases | permeability increases | permeability decreases. | increases |
| 27 | The specific heat capacity of a substance is equal to | mass of the substance × heat capacity | heat capacity ⁄ mass of the substance | mass of the substance ⁄ heat capacity | mass of the substance | heat capacity ⁄ mass of the substance |
| 28 | Specific heat capacity of glass is | 635 J kg$^{-1}$ °C$^{-1}$ | 670 J kg$^{-1}$ °C$^{-1}$ | 705 J kg$^{-1}$ °C$^{-1}$ | 740 J kg$^{-1}$ °C$^{-1}$ | 670 J kg$^{-1}$ °C$^{-1}$ |
| 29 | The specific heat capacity of a substance is equal to | the amount of heat required to raise the temperature of a 1 kg of a substance by 1 K | the amount of heat required to raise the temperature of a substance by 1 K | the amount of heat required to change the phase of a substance from solid to liquid without any chan | the amount of heat required to change the phase of a substance from liquid to gas without any change | the amount of heat required to raise the temperature of a 1 kg of a substance by 1 K |
| 30 | Specific heat capacity of mercury is | 120 J kg$^{-1}$ °C$^{-1}$ | 140 J kg$^{-1}$ °C$^{-1}$ | 160 J kg$^{-1}$ °C$^{-1}$ | 180 J kg$^{-1}$ °C$^{-1}$ | 140 J kg$^{-1}$ °C$^{-1}$ |
| 31 | The amount of heat required to raise temperature of a substance by 1°C is called as: | work capcaity | heat capacity | energy capacity | specific heat capacity | heat capacity |
| 32 | Heat capcity  does not depends on | change in temperature | mass of body | nature of substance | height of substance | height of substance |
| 33 | Heat brings ________ change | physical | chemical | reversible | periodic | chemical |
| 34 | The amount of heat required to raise the temperature of 1 kg by 1°C is called as: | work capcaity | heat capacity | energy capacity | specific heat capacity | specific heat capacity |
| 35 | SI unit of specific heat capacity is: | kg°C | j/kg°C | j/kg° | j/g°C | j/kg°C |
| 36 | Which of the following has highest heat capacity? | water | air | soil | wood | water |
| 37 | The temperature at which liquid changes into vapour is called as | Melting point | boiling point | expansion point | phase transition | boiling point |
| 38 | In Conduction process the molecules of the solid pass the heat from one to another | without themselves moving from their positions | No movement | themselves move from one place to another | without themselves moving from one place to another | without themselves moving from their positions |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 39 | The process of transfer of heat in liquids & gases is called as | Conduction | Radiation | Convection | absorption | Convection |
| 40 | Solids are not heated by convection because | solid are not free to move from one place to another | molecules only vibrate about fixed position | both A and B | they are loosely packed | both A and B |
| 41 | It is the process of heat transfer from a hot body to a colder body without heating the space between the two is called as | Conduction | Radiation | Convection | absorption | Radiation |
| 42 | The transfer of heat by radiation | does not require any medium. | require any medium | does not require any space | require any space | does not require any medium. |
| 43 | Heat of sun reach the earth by | Conduction | Radiation | Convection | absorption | Radiation |
| 44 | A cold steel spoon is dipped in a cup of hot milk. It transfers heat to its other end by the process of…………… | Conduction | Radiation | Convection | absorption | Conduction |
| 45 | Why conduction is only possible in solids | particles of solids are closely packed | heat is transferred from the hotter end to the colder end of an object | heat is transferred from the colder end to the hotter end of an object | both A and B | both A and B |
| 46 | The water is poor conductors of heat so do not heated by | Conduction | Radiation | Convection | absorption | Conduction |
| 47 | Which of the following are the examples of conductors? | plastic | Iron | wood | silicon | iron |
| 48 | Which of the following are the examples of insulators ? | copper | Iron | wood | silicon | wood |
| 49 | Radiation is the transfer of heat by means of | magnetic wave | electromagnetic waves | electrical wave | radio waves | electromagnetic waves |
| 50 | Materials which lack permanent magnetic dipoles are called | dia magnet | ferro magnet | semi-magnet | para magnet | dia magnet |
| 51 | Materials having a high dielectric constant, which is non-linear, are known as | elastomers | ferroelectric materials | super die-electrics | hard die-electrics | ferroelectric materials |
| 52 | In ferromagnetic materials | the atomic | the atomic | the constituents | one of the | the atomic |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | magnetic moments are antiparallel and unequal | magnetic moments are parallel | is iron only | constituent is iron | magnetic moments are parallel |
| 53 | The temperature beyond which substances lose their ferroelectric properties, is known as | curie temperature | critical temperature | inversion temperature | conversion temperature | curie temperature |
| 54 | What is the degeneracy of the rotational energy level with $J = 4$ for a heteronuclear diatomic molecule? | 1 | 2 | 3 | 9 | 9 |
| 55 | Which type of statistics is used to describe the electron contribution to specific heat? | MB statistics | BE statistics | FD statistics | Classical statistics | FD statistics |